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REMARKS

The present response adds new claims 18-20, and requests reconsideration of the rejected claims. Presently, claims 1-20 are pending.

Claims 1-2, 7-8, 10, and 13-17 are rejected under 35 U.S.C. 102(b) as allegedly being anticipated by Sano et al. Claims 3, 9, and 11-12 are rejected under 35 U.S.C. 103(a) as allegedly being unpatentable over Sano et al. Claim 4 is rejected under 35 U.S.C. 103(a) as allegedly being unpatentable over Sano et al. as applied to claim 1 above, and further in view of Plueddemann. Claims 5-6 are rejected under 35 U.S.C. 103(a) as allegedly being unpatentable over Sano et al. as applied to claim 1 above, and further in view of van der Kolk et al. These rejections are overcome for the reasons detailed below.

With regard to the rejections based on the art, it is again submitted that the primary reference, Sano, does not disclose coating compositions comprising a silica sol, as in the claimed invention. Accordingly, it is requested that the rejections based on Sano be withdrawn.

A technical explanation of why Sano does not disclose a silica sol can be found in the literature enclosed. In brief, it can be summarized as follows.

Sano describes that a composition is prepared by mixing an aqueous solution of alkali silicate and amorphous silica, followed by heating while stirring, see column 1, lines 52-58. Sano states at column 3, lines 5-9 that the resultant composition is a multi-component mixture comprising:

- monomeric silicate ion,
- polymeric silicate ion micelle,
- incompletely soluble amorphous silica or its hydrate, and
- amorphous silica with adsorbed silicate ions.

"Incompletely soluble amorphous silica or its hydrate" is present in Sano's system because amorphous silica powder is added. The powder has a particle size of 0.5 to 50 micron, see Sano column 4, lines 60-65. As it is incompletely soluble, this addition results in particles in the system that are present as big, micron size lumps instead of in nanometer size sols. Sano refers to this at column 4, lines 56-59 by the phrase "mixed compositions of alkali silicate and amorphous silica powder". Hence, the "incompletely soluble amorphous silica or its hydrate" is not a sol.

Further, the composition comprises a mixture of "monomeric silicate ion", "polymeric silicate ion micelle", and "amorphous silica with adsorbed silicate ions". Iller (enclosed) refers to solutions comprising a mixture of particles of molecular dimensions to particles up to 5 nm as "polysilicates", see Iller Chapter 2, page 116, paragraphs 2-4.

Since a polysilicate differs from a sol, Sano does not describe a binder, wherein the binder comprises an aqueous silica sol.

The difference between a polysilicate solution and an alkali stabilized sol of colloidal silica is described by Iller by indicating the borderline between the two types of systems, see Iller Chapter 2, page 143, paragraph 6, to page 144, paragraph 2 as follows:

"The borderline between a polysilicate solution and an "alkali-stabilized sol of colloidal silica" can be drawn at the particle size of the silica below which the increased solubility of the silica as $\text{Si}(\text{OH})_4$ causes the particles to grow spontaneously unless more alkali is added. However, when particles less than 5 nm in size are stabilized against growth by adjusting the ratio to less than 25:1 [$\text{SiO}_2/\text{Na}_2\text{O}$ system], an increasing and substantial fraction of the silica is converted to silicate ions. Thus a "polysilicate" solution may be considered to be an equilibrium mixture of ionic and negatively charged particles of colloidal silica of such extremely small size that they can be classed also as polyanions."

Hence, in a sol system discrete silica particles are present and due to the "spontaneous growth" (sometimes referred to as Ostwalt ripening), a silica sol hardly comprises particles of molecular dimensions. After all, these would grow together with the sols.

A polysilicate system (for Sano the mixture of "monomeric silicate ion", "polymeric silicate ion micelle", and "amorphous silica with adsorbed silicate ions"), on the other hand, contains much more alkali than necessary to stabilize sols of the smallest particle size manufactured and sold as colloids. See Iller Chapter 2, page 143, paragraph 5. This results in the above-described partial conversion into silicate ions.

In conclusion, Sano's system does not comprise a sol, as claimed herein.

General information on silicate systems can be found in the following enclosed documents:

- R.K. Iller, "The chemistry of silica", John Wiley & Sons, New York, 1979, chapter 2, page 116-137 + page 142-149
- R.K. Harris et al., J. Am. Chem. Soc., **1981**, *103*, 1577-1578
- L.S. Dent Glasser, Chemistry in Britain, January **1982**, 33-39
- L.S. Dent Glasser, J.C.S. Dalton, **1980**, *part I and II*, 393-402
- Details on silicate solutions sold by Crossfield Chemicals

General information on silica sols can be found in the following enclosed documents:

- R.K. Iller, "The chemistry of silica", John Wiley & Sons, New York, 1979, chapter 4, page 312 –418
- A. Yoshida, "The colloid chemistry of silica", Am. Chem. Soc., 1994, chapter 2, page 51-66
- Details on Ludox silica sols ex Grace Davison

New claims 18-20 are substantially the same as claims 1, 13 and 14, respectively, except that they include zinc powder or a zinc alloy and also recite a silica sol having a particle size in the range of 3 to 100 nm and having a SiO₂/M₂O mole ratio, where M represents total alkali metal and ammonium ions, of at least 25:1. Support for these claims can be found in the specification, for example, 4, lines 18-22, page 6 lines 24-32, and page 13 lines 27-29.

Entry of these new claims is requested pursuant to 37 CFR 1.116 to place the application in better form for consideration in the event an appeal is necessary. New claims 18-20 are patentable over Sano for the same reasons claims 1-17 are patentable as well as for the inclusion of zinc powder or a zinc alloy, which is not taught or suggested by Sano.

A Notice of Appeal is filed concurrently herewith to ensure the pendency of the application while the present response is considered.

Respectfully submitted,



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CHAPTER 2

Water-Soluble Silicates

Vail's two-volume monograph on soluble silicates (1) after a quarter of a century is still the primary source of technical and industrial information. It is pertinent to review some of the advances made since then in the chemistry of soluble silicates, from which silica colloids and gels are largely derived.

Silicate and polysilicate ions are still not well understood. The main distinction between polysilicate ions and very small negatively charged colloidal silica particles is probably one of terminology. In the past, solutions of alkali metal silicates obtained by dissolving sodium or potassium silicate glasses in water seemed to be clearly distinct from sols of colloidal silica stabilized with a minor amount of alkali. Silicate solutions were made by dissolving glasses with $\text{SiO}_2:\text{Na}_2\text{O}$ ratios less than 4:1. Since these glasses with more silica and less alkali do not dissolve, silicate solutions of higher ratios were not available.

On the other hand, when it was learned how to make silica particles of different sizes it was found that smaller particles could be stabilized as sols by adding more alkali. Thus 5 mm particles were stabilized with a ratio of 25:1. However, attempts to obtain concentrated solutions with still smaller particles and lower ratios of 25:1 to 4:1 led to gelled mixtures when sodium hydroxide was used as the alkali. Then it was found that such solutions could be made using other alkalis so that solutions containing particles smaller than 5 nm, on down to molecular dimensions, were obtained.

Solutions in this range are referred to here as "polysilicates," with the understanding that these polyanions may at the same time be treated as very small charged particles.

Further study of this question was simplified when it was recognized that the sodium ion was unusual in its influence on the gelling behavior of the system. Solutions in this intermediate ratio range made with a potassium, lithium, or tetramethylammonium base proved to be more stable in regard to thickening and gelling. Other stabilizing cations were guanidinium and ethylenediamine copper.

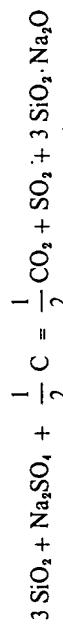
Over the past 50 years there have been major changes in theories of the nature of the silica in the conventional alkali silicate solutions with $\text{SiO}_2:\text{Na}_2\text{O}$ ratios from 2:1 to 4:1. The physical similarity of viscous, "stringy" solutions of soluble silicates to solutions of linear organic polymers led in some cases to the supposition that vis-

SODIUM AND POTASSIUM SILICATES

Manufacture

It has been known since the seventeenth century that sand and sodium or potassium carbonate react at red heat to form a water-soluble glass called "water glass." As noted by Vail (1), Johann Nepomuk von Fuchs was the first to investigate alkali silicates systematically and even before 1850 proposed their uses as adhesives, cements, and fireproof paints. By 1855 water glass was being made commercially, both in Europe and America.

Manufacture has generally been carried out in large open-hearth furnaces above 1300°C by the following reactions:



Except under unusual circumstances, the latter reaction using "soda ash" is always employed.

The manufacture of soluble silicates was reviewed by Williams (2). Improvements in reaction furnaces have been proposed. Burke (3) discloses coating sand particles with a mixture of sodium silicate and NaOH to give a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2.5:1 to 4:1 and heating the particles in suspension in a flame to more than 3500°F, at which temperature uniform particles of soluble glass are formed. Other proposals are a cyclone type furnace (4), a vertical column furnace in which reactants pass downward into a heated reactor and the product moves upward around the column as a heat exchanger (5), and a submerged combustion furnace in which a 70% reduction in fuel cost and 80% reduction in size can be realized (6). Quantitative data on the rate of dissolution of sand (quartz) in molten Na_2SiO_3 or $\text{SiO}_2\text{-Na}_2\text{O}$ glass have become available. Terai, Sugae, and Hayami (7) found that at atmospheric pressure the reaction product at the SiO_2 -molten Na_2CO_3 boundary is metasilicate, whereas under vacuum the reaction rate is slower and metasilicate is not detected. Diffusion

Commercial Solutions

Properties and uses of soluble silicates have been summarized by Weldes and Lange (19). Typical commercial (American) solutions are listed in Table 2.1. The key variables in silicate solutions are the following:

1. The alkali metal.
2. The ratio of SiO_2 to alkali metal oxide expressed by either weight or molar ratio. In the case of sodium silicate the two ratios are nearly identical.
3. The concentration of solids.

Minor improvements in the clarity and purity of solutions continue to be made. For example, Tauch found that if sodium silicate glass of 3.25 ratio is dissolved in water in an autoclave to too high a concentration, the resulting solution becomes turbid. By stopping at a concentration corresponding to 38°Be and then vacuum concentrating to 41°Be, a clear concentrated product is obtained (11). To obtain a clearer solution of sodium silicate, Rathmell disclosed adding TiO_2 to the glass-batch to give a concentration in the melt of 400–3000 ppm (12). Apparently the presence of 4 moles of TiO_2 per gram-atom of calcium prevents the later formation of insoluble calcium silicates.

The use of sodium salts other than carbonate is still of limited interest. In 1941, Ille and Tauch (13) studied the equilibrium

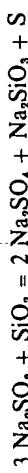


and found $K = [\text{HCl}]^2[\text{NaCl}]^{-2}[\text{H}_2\text{O}]^{-1} = +2.9$ at 1000°C.

Calculations showed the impossibility of producing HCl at a practical concentration while obtaining a reasonable conversion based on NaCl. The equilibrium is more favorable under 1000°C, but the reaction rate is very low. In 1972, Hanf and Sole (14) reexamined the reaction at lower temperatures down to 700°C, and concluded that the equilibrium constant was favorable to using the reaction for processing certain copper ores containing silica.

Sodium sulfate reacts with sand even in an oxidizing atmosphere at 1400°C if reactants are spread in a very thin layer (0.5 mm). However, under reducing conditions (presumably CH_4) the reaction proceeds at 900°C with production of H_2S (15).

Sodium sulfate in a closed system reacts with silica at 700–900°C as follows (16):



When the cost of NaOH relative to NaCO_3 is favorable, silicate solutions with $\text{SiO}_2:\text{Na}_2\text{O}$ ratios up to 2.0 or 2.5 can be made directly by autoclaving sand with strong NaOH solution. According to Ordiales (17) if hydrated or microcrystalline silicas such as opal, chalcedony, diatomite, or tripolite are available, it is possible to produce a solution with ratio as high as 3.22. The system water–silica–sodium monoxide has been examined by Morey and Hesselgesser (18) at pressures up to 2500 bars and 400°C. The solid phases are Na_2SiO_3 , $\text{Na}_2\text{Si}_2\text{O}_5$, and quartz.

Table 2.1. Composition of Typical American Commercial Alkali Metal Silicate Solutions

| Alkali Metal | Wt. Ratio $\text{SiO}_2:\text{M}_2\text{O}$ | SiO_2 (%) | Na_2O (%) | Density (lb/gal) | Viscosity (centipoise) |
|--------------|---------------------------------------------|--------------------|---------------------------|------------------|------------------------|
| Sodium | 3.75 | 25.3 | 6.75 | 11.0 | 220 |
| | 3.25 | 29.9 | 9.22 | 11.8 | 830 |
| | 3.25 | 28.4 | 8.7 | 11.6 | 160 |
| | 3.22 | 27.7 | 8.6 | 11.5 | 100 |
| | 2.87 | 32.0 | 11.1 | 12.4 | 1,250 |
| | 2.58 | 32.1 | 12.5 | 12.6 | 780 |
| | 2.50 | 26.5 | 10.6 | 11.7 | 60 |
| | 2.40 | 33.2 | 13.85 | 13.0 | 2,100 |
| | 2.20 | 29.2 | 13.3 | 12.5 | — |
| | 2.00 | 29.4 | 14.7 | 12.8 | 400 |
| | 2.00 | 36.0 | 18.0 | 14.1 | 70,000 |
| | 1.90 | 28.5 | 15.0 | 12.7 | — |
| | 1.80 | 24.1 | 13.4 | 12.0 | 60 |
| Potassium | 1.60 | 31.5 | 19.7 | 14.0 | 7,000 |
| | 2.50 | 20.8 | 8.3 | 10.5 | 40 |
| | 2.20 | 19.9 | 9.05 | 10.5 | 7 |
| | 2.10 | 26.3 | 12.5 | 11.5 | 1,050 |

assembled by Weldes and Lange (19). A few further observations are here noted as follows, although a thorough literature search was not made.

The specific gravity of a silicate solution is used to determine concentration, if the ratio is known. Otherwise, analysis for silica or alkali is required. Shtyrenkov et al. (20) propose titrating the normality of the alkali, from which the molar ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ can be determined as $55.16(d - 1)N = 2.28$ where d is specific gravity and N is alkali normality.

Measurements have been made of certain physical properties of sodium silicate solutions over a wide range of ratios and concentrations. Accurate pH data have been published by Bacon and Wills (21), who used specially designed electrode cells. Densities of the solutions were also reported and an empirical equation given:

$$d = 1 + aA + bA^2 + cA^3$$

where d = specific gravity, $20^\circ\text{C}/20^\circ\text{C}$
 A = wt. % Na_2O in the solution

and a , b , and c are constants that vary with the molar ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ which, however, covered only the range from 1.3 to 0.5.

Electrical conductivity was measured by Ukihashi (22) on solutions ranging in $\text{SiO}_2:\text{Na}_2\text{O}$ ratio from 1.0 to 3.95 and concentrations from 10^{-3} N to maximum viscosity.

The viscosity of 3.41 ratio sodium silicate solutions was measured by Grant and Masson (23) over the concentration range of $0.005\text{--}0.3253 \text{ g ml}^{-1}$ and the intrinsic viscosity (specific viscosity divided by concentration) was found to be independent of the shear rate. At a concentration of 0.325 g ml^{-1} the intrinsic viscosity was 16 ml g^{-1} ; at 0.02 g ml^{-1} it was 3.2 ml g^{-1} , and at zero concentration the extrapolated value was 3.1 ml g^{-1} . This demonstrated that the silicate ions were of low molecular weight and lacked chainlike character even in dilute solution.

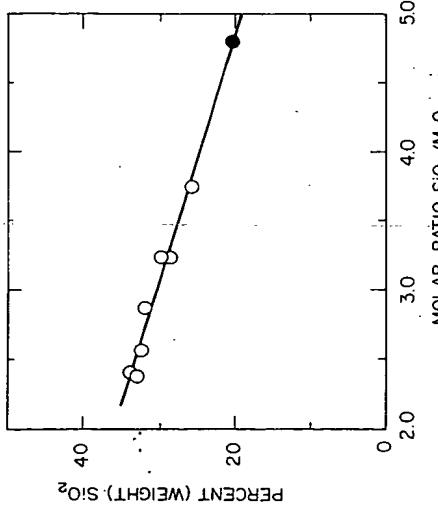


Figure 2.1. Maximum concentration of SiO_2 for a pourable viscosity of silicate solution versus molar $\text{SiO}_2:\text{M}_2\text{O}$ ratio, O , $\text{M} = \text{Na}; \bullet, \text{M} = \text{Li}$.

Soluble Crystalline Sodium and Potassium Silicates

Sodium metasilicate nonahydrate $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (m.p. 47°C) is the only form made chemically pure for use as a standard. For industrial uses, both anhydrous Na_2SiO_3 and $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ are produced along with other more highly alkaline grades.

The following anhydrous crystalline forms, obtained from the melt, have a $\text{SiO}_2:\text{M}_2\text{O}$ ratio of 1 or higher:

| Silicate | M.p. ($^\circ\text{C}$) |
|------------------------------------|---------------------------|
| Na_2SiO_3 | 1089 |
| $\text{Na}_2\text{Si}_2\text{O}_5$ | 874 |
| K_2SiO_3 | 976 |
| $\text{K}_2\text{Si}_2\text{O}_5$ | 1045 |
| $\text{K}_2\text{Si}_4\text{O}_9$ | 770 |

There are numerous hydrates of meta- and disilicates, as listed by Vail (1), but $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (m.p. 72.2°C) is the principal commercial product.

Properties of Solution

The properties of sodium silicate solutions at all ratios and concentrations have been described in detail by Vail (1) in 1952. A very convenient summary of data on key properties such as phase diagrams, pH, density, viscosity, and solubility has been

1. Cleaners and detergents that depend on controlled alkalinity are made generally from silicates with molar $\text{SiO}_2:\text{Na}_2\text{O}$ ratios less than 2.5, especially meta- and orthosilicates.

2. Adhesive, binder, and deflocculant applications, which depend on the presence of polysilicate ions, require silicates generally with ratios from 2.5 to 3.8. For maximum adhesive strength the lower ratio types are used because they can be obtained with a higher concentration of solids. For more water resistant bonds, the higher ratios are needed.

3. For the production of precipitated silicas, sols, and gels, sodium silicate of ratio about 3.3 is usually used rather than lower ratios, since less acid is required for neutralization of alkali per unit of silica, and this ratio is available at low cost because such large volumes are produced. However, the 3.8 ratio may be used to some further advantage if acid consumption is an important factor in cost.

For each particular application, specific grades of carefully selected ratio and concentration (viscosity) are recommended by the manufacturers.

Trends in uses will no doubt change as organic binders and adhesives become more expensive relative to sodium silicate. Over the last 40 years, starch replaced much of the silicate adhesives used in making corrugated boxboard, but the trend may be reversed. Resins used as binders in foundry molds and cores become less economic with increasing raw material costs and the necessity to reduce atmospheric pollution. Replacement by silicate apparently is becoming attractive as new means of rapid set are devised (24). Fast setting by carbon dioxide, used in a limited way for many years, may become universal (25). The use of silicate as a binder in cores has posed problems not encountered with resins, which burn out easily. The addition of amorphous silica along with silicate binder permits the development of a strong cristobalite-rich bond at high temperature, which disintegrates when cooled below 200°C, according to Yates (26).

Sodium silicates used as adhesives have $\text{SiO}_2:\text{Na}_2\text{O}$ ratios in the range 2:1 to 4:1. A ratio of 3.3 is most commonly used on products of paper or asbestos. At ratios of 2 or less, adhesive bonds are weaker and very water sensitive. At ratios above 4.0 (polysilicates) the adhesive strength is less, although water resistance is better. Since at a workable viscosity, the solids content increases with decreasing ratio, silicate of ratio 2 and of high concentration is used in dense products such as grinding wheels, where water is hard to remove and highest bond strength is needed.

As is discussed later, the silicate adhesive solution of ratio 3.3 may be thought of as a solution of ratio 2 consisting of Na^+ and HSiO_3^- ions in which the remaining silica is suspended as exceedingly small colloidal particles 1–2 nm in diameter. At higher ratios, there is a decreasing proportion of ionic silica.

It is observed that when silicate solutions of increasing ratios are spread as uniform thin films on glass and dried, the films crack or craze beyond a certain ratio. This assumes uniform film-forming and drying conditions, since film thickness, rapidity of drying, and temperature can all influence the degree of crazing. The greater the degree of crazing or micro-cracking, the less strength the silicate exhibits as an adhesive.

It is probable that crazing occurs when the volume of dried NaHSiO_3 is insufficient to fill the spaces or pores between the spherical colloidal particles as they become packed together upon drying. If the residual solid ionic silicate does not fill the pores, then the gel-like network of particles shrinks, and cracks develop in the film. Thus the greater the tendency to micro-crack, the lower the strength of the dried film.

It is possible to calculate the relative volumes of NaHSiO_3 and colloid present in dried silicates of different ratios. It will be assumed that NaHSiO_3 solution dries to

its indicated composition, in which case its density is about 2.0 g cm^{-3} . The silica particles of about 11 Å diameter contain 23% H_2O and 77% SiO_2 , and have a density of 1.72 (Chapter 1). It is assumed that when the silicate is dried, the sodium ions are coordinated with the oxygen atoms and silanol groups in the system and there is no water bonded to the sodium ions. When a suspension of small spheres is dried, the particles are randomly packed with a packing density about 50% by volume.

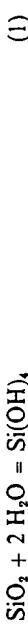
To meet the above postulated requirement that the pores must be filled to avoid crazing, the final volume of dried NaHSiO_3 must equal that of the colloidal particles. This in turn requires, for 100 cm³ of dried adhesive, 85 grams of the colloid (19.5 grams H_2O and 64.5 grams SiO_2) and 100 grams of NaHSiO_3 , (31 grams Na_2O , 60 grams SiO_2 , 9 grams H_2O). This overall composition has a $\text{SiO}_2:\text{Na}_2\text{O}$ weight ratio of 4.0:1, or a molar ratio of 4.13. This is in agreement with the observation that sodium or lithium silicate solutions of ratio higher than 4, generally called "polysilicates" in commerce, do not dry to clear, continuous films as do solutions of lower ratio because micro-cracking occurs.

It should be pointed out that such a composition of 50 vol. % solids dried to an extremely brittle state before the last of the water is removed. In considering the behavior of fillers in plastics, for example, more than about 40% by volume gives a hard, relatively brittle mass. Likewise, less than 40% by volume of colloid in silicate should give a less brittle film as the last of the water is removed. In this case, by similar calculations it is found that this corresponds to a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 3.5. Perhaps by coincidence this is near the common ratio used in adhesives.

It seems, therefore, that at least some of the behavior of soluble silicates with ratios greater than 2 is consistent with the theory that the solutions consist of NaHSiO_3 in solution along with very small particles of colloidal silica with silanol surfaces.

THE NATURE OF SILICATE SOLUTIONS

The fundamental equilibria involved have in the past been listed as follows:



For the above equations at 25°C, taking the ionization constant of water as 10^{-14} :

$$\frac{[\text{H}^+][\text{HSiO}_3^-]}{[\text{Si(OH)}_4]} = 10^{-9.8} \quad \text{or} \quad \frac{[\text{OH}^-][\text{Si(OH)}_4]}{[\text{HSiO}_3^-]} = 10^{-4.2}$$

$$\frac{[\text{H}^+][\text{SiO}_3^{2-}]}{[\text{HSiO}_3^-]} = 10^{-12.16} \quad \text{or} \quad \frac{[\text{OH}^-][\text{HSiO}_3^-]}{[\text{SiO}_3^{2-}]} = 10^{-1.64}$$

$$\frac{[\text{H}^+][\text{Si}_2\text{O}_6^{4-}]}{[\text{HSi}_2\text{O}_6^-]} = 10^{-0.8} \quad \text{or} \quad \frac{[\text{OH}^-][\text{HSi}_2\text{O}_6^-]}{[\text{Si}_2\text{O}_6^{4-}]} = 10^{-4.2}$$

$$\frac{[\text{H}^+][\text{HSi}_2\text{O}_6^-]}{[\text{Si}_2\text{O}_6^{4-}]} = 10^{-12.8} \quad \text{or} \quad \frac{[\text{OH}][\text{Si}_2\text{O}_6^{4-}]}{[\text{HSi}_2\text{O}_6^-]} = 10^{-1.20}$$

$$\frac{[\text{Si}_2\text{O}_6^{4-}]}{[\text{HSiO}_3^-]} = 2200$$

The above constants were measured by Roller and Ervin (27) in a system involving calcium as the base. There is now some doubt whether disilicate ions are formed in sodium silicate solution in accordance with the above equations. My observations indicate that in the presence of colloidal particles and at very low sodium ion concentration, only HSiO_3^- and SiO_3^{2-} are in equilibrium with Si(OH)_4 and OH^- ions. A 1% sol of very small particles of colloidal silica was made by polymerizing monosilicic acid made from ethyl silicate, for 24 hr at 25°C, at pH 7.8. There was some increase in pH as the specific surface area, determined by the Sears method (28), dropped to 1040 $\text{m}^2 \text{ g}^{-1}$ as the silica particles grew to about 2.6 nm in diameter. To portions of this sol NaOH solution was added to adjust pH to various values between 8.5 and 10.5. These sols were then aged at 25°C while small samples were taken repeatedly to measure the rate of color development with molybdic acid reagent. After 2 hr aging, no further changes were noted in the reaction rates in the different samples. The amounts of silica reacted at indicated times are shown in Figure 2.2. After about 5 min, the slopes of all the curves are alike and correspond to the rate of reaction of the colloidal particles with molybdic acid. As a matter of interest, the rate of reaction was about 300 mg $\text{SiO}_2 \text{ hr}^{-1}$ per 10^4 mg of total silica in the sample, which had a total surface area of 10,400 m^2 . The specific rate was $3 \times 10^{-5} \text{ g m}^{-2} \text{ hr}^{-1}$.

By extrapolating the linear portions of curves in Figure 2.2 to zero time, the total concentrations of soluble, that is, monomeric and ionic, silica in the original sol samples were determined:

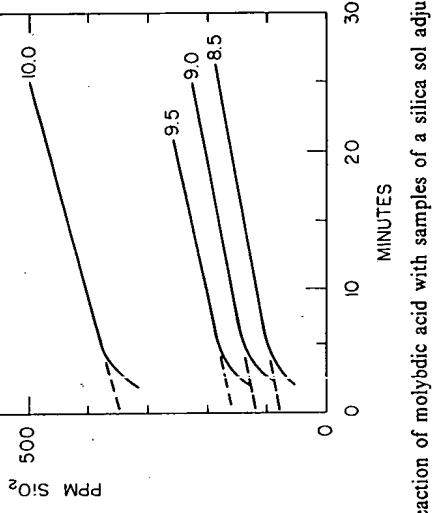


Figure 2.2. Reaction of molybdic acid with samples of a silica sol adjusted to various pH, indicated on each curve.

From Figure 1.10b, line B, the equilibrium solubility of 2.6 nm particles at pH 8 is indicated to be about 150 ppm or 2.5 mM; this is reasonably close to the value extrapolated to pH 8 from the above data (see Figure 2.3).

Taking this value of 2.5 mM for the concentration of Si(OH)_4 , and Roller's and Ervin's equilibrium constants, it is possible to calculate the concentration of the various species at equilibrium.

$$[\text{HSiO}_3^-] = [\text{Si(OH)}_4][\text{H}^+]^{-1} \times 10^{-0.8}$$

$$[\text{SiO}_3^{2-}] = [\text{HSiO}_3^-][\text{H}^+]^{-1} \times 10^{-12.16}$$

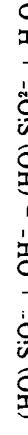
$$[\text{Si}_2\text{O}_6^{4-}] = 2200[\text{HSi}_2\text{O}_6^-]^2$$

$$[\text{HSi}_2\text{O}_6^-] = [\text{Si}_2\text{O}_6^{4-}][\text{H}^+] \times 10^{+9.8}$$

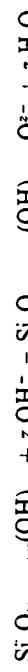
Calculated concentrations of Si(OH)_4 , HSiO_3^- , and SiO_3^{2-} are plotted cumulatively for various pH values in Figure 2.3. Although the curves are somewhat different at

| pH of Sol | Monomeric and Ionic SiO_2 | |
|-----------|------------------------------------|------|
| | ppm | mM |
| 8.5 | 175 | 2.9 |
| 9.0 | 220 | 3.7 |
| 9.5 | 260 | 4.3 |
| 10.0 | 450 | 7.5 |
| 10.5 | 950 | 15.8 |

atoms in the interior are linked only to other silicon atoms by oxygen atoms, but each silicon atom on the exterior bears at least one OH group. These particles are in solubility equilibrium with soluble silica monomer, Si(OH)_4 , which in turn is in equilibrium with monomeric silicate ions. The particles are also negatively charged by partial ionization of the surface OH groups to SiO^- anionic sites.



where x is the ratio $\text{OH}:\text{Si}$ that decreases as the degree of polymerization, n , increases. Upon raising the pH, ionization occurs:



where z is the number of charges on a polymer containing n silicon atoms.

Although it has long been known that polymeric silicate ions are present in such silicate solutions, it has not previously been suggested that such polymeric species be considered as silica particles in solubility equilibrium with Si(OH)_4 in accordance with the Ostwald-Freundlich equation relating diminishing particle size to increasing solubility. It is suggested that the equation may be at least approximately followed even by spherical particles as small as 10-20 Å in diameter, where a large fraction of the silicon atoms are on the surface.

The existence of such small dense charged silica particles would appear improbable were it not for the fact that particles of this type are known to exist as discrete ions containing as few as eight silicon atoms. As discussed later in connection with the structure of certain crystalline silicates, it is definitely possible for silica to form a compact octameric structure (HOSiO_4)₈ in which the silicon atoms are at the eight corners of a cube, each being linked through oxygen atoms to three other silicon atoms and each having one SiOH group which may ionize to give the polyion $(\text{Si}_8\text{O}_{20})^{4-}$ (Figure 2.6). This unit is the beginning of a colloidal "particle" that is about 1 nm in diameter. However it is only after it is surrounded by further condensation of monomer that it becomes a "silica particle" having a core of SiO_4 .

From the various cyclic polysilicate ions that exist in small amounts in solution as the $\text{SiO}_4:\text{Na}_2\text{O}$ ratio exceeds 2:1, similar polycyclic oligomers appear as the first three-dimensional particulate "colloid" species. These then serve as nuclei as still larger colloid-ion species are formed at higher $\text{SiO}_4:\text{Na}_2\text{O}$ ratios.

In my earlier book (29), I suggested possible structures of polysilicate ions on the assumption that the silicon might have a coordination number of six. Baker, Jue, and Wills had earlier proposed that polysilicate ions might thus be analogous to isopoly- or heteropolyacid anions (30). However, current evidence indicates that silicon still has a coordination number of four toward oxygen in silicate ions, as will be further

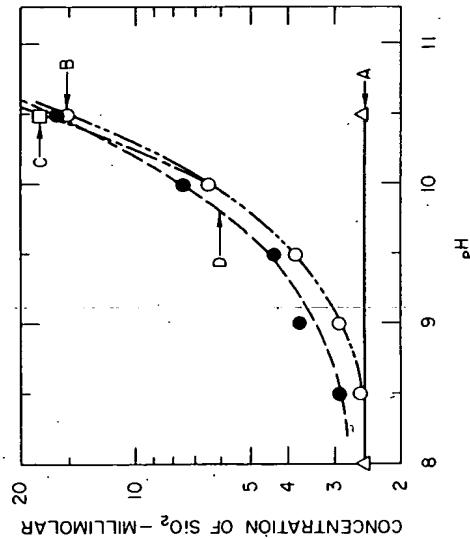


Figure 2.3. Concentration of soluble silica species in equilibrium with 2.6 nm diameter silica particles at pH 8.5-10.5: A, Si(OH)_4 , in equilibrium with 2.6 nm particles; B, calculated total concentrations of Si(OH)_4 and HSiO_3^- ; C, calculated total concentrations of Si(OH)_4 , HSiO_3^- , and SiO_3^{2-} ; D, observed total soluble silica.

pH 9, it is clear that at pH 10.5, the total concentration of soluble silica can be accounted for by Si(OH)_4 and HSiO_3^- , with possibly a small amount of SiO_3^{2-} . Thus no other ionic species can be present in appreciable amounts.

According to the above equations, the disilicate ions $\text{Si}_2\text{O}_5^{2-}$ and HSi_2O_5^- should also be present in much higher concentrations than HSiO_3^- . Since it is well known that disilicic acid reacts completely with molybdic acid in less than 5 min, the total silica reacting in 5 min should have been much higher than observed if the equations relating to disilicate ions were applicable to the present system.

It is therefore concluded that Roller's and Ervin's (27) observations regarding the formation of disilicate ions were valid only in the calcium silicate system in which their studies were made. It would not be surprising to find that the divalent calcium ion promotes the formation of complex disilicate ions in which Si-O-Ca linkages are involved.

Theory

A concentrated solution of sodium or potassium silicate with $\text{SiO}_4:\text{M}_2\text{O}$ molar ratios of 1:1 to 1:2 consists mainly of SiO_3^{2-} and HSiO_3^- ions. However, in solutions of higher ratios it is proposed that an increasing proportion of the silica forms extremely small three-dimensional, internally condensed silicate polymer-ions or charged particles. These are generally equiaxed or spheroidal in shape. The silicon

discussed. Accordingly, the present theory does not involve 6-coordinated silicon in any way.

The size of the polymeric or colloidal species in sodium silicate solutions can be estimated from various available data according to the foregoing theory, and can also be determined directly by several means including ultrafiltration, rate of reaction, and conversion to stable species which can be isolated.

According to Bacon and Wills (21) accurate pH values were measured on a silicate of $\text{SiO}_2:\text{Na}_2\text{O}$ molar ratio 3.36 and were reported at different concentrations of Na_2O in solution. Since the ratio of SiO_2 to Na_2O was constant, the silica concentrations are also known. Using the foregoing theory it is possible to estimate the particle size of the polymeric silica from its solubility, that is, from the concentration of $\text{Si}(\text{OH})_4$ present.

Referring to symbols defined in Table 2.2, and assuming that the only silicate ion present is HSiO_3^- ,

$$S_t = M + M'$$

$$K_1 = \frac{MH}{M'} = 10^{-4.2} \text{ (value listed earlier)}$$

$$M = \frac{K_1 M'}{H} = K_1 \frac{A - H}{H}$$

For solutions containing 0.7–0.10% Na_2O the value of $H/(A - H)$ is relatively constant and averages 0.008. This also indicates that all the silica can be accounted for as $\text{Si}(\text{OH})_4$ and HSiO_3^- and that no disilicate is present. From this the concentration of $\text{Si}(\text{OH})_4$ can be calculated:

$$M = 10^{-4.2} \frac{M'}{H} = 10^{-4.2} \frac{A - H}{H}$$

whence M is $10^{-2.1}$ or $0.0079 M$, or 474 ppm as SiO_2 .

This value remains relatively constant over a sevenfold range of concentration. It is assumed that 474 ppm is the equilibrium solubility of the postulated colloidal silica component in silicate of molar ratio 3.36. From the formulas in Chapter 1 relating particle diameter to solubility (Figure 1.10b), the solubility is that of silica particles about 11 Å in diameter. From equations relating size to molecular weight, this corresponds to a molecular weight of $1.15 \times 10^{-21} d^3 \times 6 \times 10^{23}$, or 920, or about 15 silicon atoms per particle.

It is known that such polymeric species are present only when the molar ratio exceeds about 2 $\text{SiO}_2:\text{Na}_2\text{O}$. Hence in a solution of ratio 3.3, about $(3.3 - 2.0)(3.3)^{-1}$, or 39%, of the silica is polymeric, whereas 61% is mostly monomeric. If the degree of polymerization of the higher molecular weight fraction is about 15,

Table 2.2. pH of Sodium Silicate Solutions^a

| % Na_2O | A | pH | H | M' | H | | S_t (molar SiO_2) |
|-------------------------|--------|-------|---------|-------|---------|-------------|----------------------------------|
| | | | | | $A - H$ | $H/(A - H)$ | |
| 0.7 | 0.226 | 11.20 | 0.00158 | 0.224 | 0.00705 | 0.380 | |
| 0.35 | 0.113 | 11.00 | 0.00100 | 0.112 | 0.00892 | 0.190 | |
| 0.25 | 0.0806 | 10.80 | 0.00063 | 0.080 | 0.00788 | 0.1354 | |
| 0.15 | 0.0484 | 10.60 | 0.00040 | 0.048 | 0.00829 | 0.0813 | |
| 0.10 | 0.0323 | 10.40 | 0.00025 | 0.032 | 0.00784 | 0.0543 | |
| Average | | | | | 0.008 | | |

Source. Data from Bacon and Wills (21).

^a A = normality of total alkali in the solution; H = normality of $\text{OH}^- = 10^{14-\text{pH}}$; S_t = total silica concentration as moles SiO_2 per liter; R = molar ratio of $\text{SiO}_2:\text{Na}_2\text{O} = 3.30$; $R = 2S_t/A$ and $S_t = 1.68 A$; M' = normality of HSiO_3^- ; M = molarity of $\text{Si}(\text{OH})_4 = K_1(A - H)/H$, where $K_1 = 10^{-4.2}$.

then one can calculate the number-average and weight-average molecular weights, which are 180 and 284. These values are at least of the same order of magnitude as the number-average molecular weight 280 found by Iler (63) by a cryoscopic method, and the weight-average molecular weight 325 found by Debye and Nauman (37) by light scattering. Aveston's (31) value of 900 by equilibrium centrifugation is probably higher because he measured the molecular weight in sodium chloride solutions. Extrapolation of his data at the lowest salt concentration (0.08 M) suggests a molecular weight of about 600 for this $\text{SiO}_2:\text{Na}_2\text{O}$ ratio; in the absence of salt it would be still lower.

The question might be raised why the polysilicate fraction should not consist of a wide range of polyion or particle sizes. However, if this were the case, since the smaller particles are more soluble than the larger, rapid redistribution of silica would occur until all the charged particles were within a relatively uniform size range.

Ultrafiltration is another method by which at least an approximate idea of polymer size can be obtained. In an unpublished preliminary study, Iler used ultrafilter membranes having pores of known diameters.

The silicate solution is somewhat diluted, aged, clarified, and ultrafiltered in a rapidly stirred pressure cell at 50 psi. By following the concentration of SiO_2 and Na_2O in the filtrate one can calculate by difference how much of the silicate is polymerized to a size that will not go through the pores. Also, it can be shown that $\text{Si}(\text{OH})_4$ and HSiO_3^- pass freely through the membrane so that the initial concentration of these species in the filtrate is the same as in the initial solution. The commercial sodium silicate solutions were diluted with an equal volume of water, aged about a week, filtered through fine filter paper to remove traces of suspended matter, and then ultrafiltered.

With sodium silicate of 3.75 ratio the following observations were made:

| Nominal Pore Diameter of Membrane (Å) | % of Silica too Large to Pass |
|---------------------------------------------|----------------------------------|
| 18 | 38 |
| 24 | 25 |
| 33 | 15 |
| 52 | 0 |

In another series of tests using a single type of membrane with 18 Å pores, solutions of different ratios were tested:

| Molar Ratio $\text{SiO}_2 : \text{Na}_2\text{O}$ | % of Silica too Large to Pass Pores of 18 Å Diameter |
|-----------------------------------------------------|---------------------------------------------------------|
| 2.4 | 7 |
| 3.25 | 14 |
| 3.75 | 25 |
| $\text{SiO}_2 : \text{K}_2\text{O}$ | |
| 3.9 | 25 |

In a further study by Iler a 3.25 ratio sodium silicate solution was diluted to 6% SiO_2 and diluted suddenly to 3% by addition to an equal volume of acid, giving a pH of 2. Ultrafiltration showed that about half of the silica would not pass a 24 Å filter. Only 7% of the silica remained as monomer.

As will be shown later, esterification of such silicic acid with *n*-BuOH gave an organosol that from the composition was calculated to consist of particles about 23 Å in diameter. Apparently when the silicate was acidified the monomer added rapidly to the colloidal nuclei already present. Since 14% of the silica had been particles of 11 Å size they would grow by addition of monomer to a calculated size of $11 \times (93/14)^{1/3}$ or 21 Å diameter, which is in reasonable agreement with the size calculated from the organosol.

The main conclusion is that colloidal species are present in solutions of sodium silicates having $\text{SiO}_2 : \text{Na}_2\text{O}$ ratios greater than 2:1 and that at higher ratios a greater proportion of the silica is present as polysilicate ions or particles generally smaller than 30 nm diameter.

These observations are consistent with the foregoing theory that the particles are in solubility equilibrium with $\text{Si}(\text{OH})_4$, which in turn is in equilibrium with HSiO_3^- .

Physical Studies

It is true that the results of some investigations in the past led to the conclusion that dimeric species were present in sodium silicate solutions. Thus measurements of dif-

fusion rates of silicate ions by Jander and Jahr (32) in 1940 and still earlier by Jander and Heukeshoven (33) indicated SiO_3^{2-} is the principal ion present above pH 13.6, but between 13.6 and 10.9 the main ion present is disilicate, $\text{Si}_2\text{O}_6^{2-}$; below pH 10.9 polymeric ions are also present, whereas below about 9.0 the silica exists mainly as colloidal particles in equilibrium with $\text{Si}(\text{OH})_4$.

However, it is possible that the lower diffusion rate ascribed to $\text{Si}_2\text{O}_6^{2-}$ might be due to HSiO_3^- hydrogen-bonded to water molecules, or to a loosely hydrogen-bonded $[\text{O}_3\text{Si}(\text{OH})_2\text{SiO}_3]^{2-}$ complex and not to the formation of an oxygen-bonded dimeric ion. In any case, the exact nature of the dimer ions in silicate solutions, if present, remains to be determined.

Most investigators, especially since 1950, indicate that in aqueous 3:3:1 ratio sodium silicate solutions there are few dimer and trimer ions and the silica is distributed between monomers, HSiO_3^- or SiO_3^{2-} , and three-dimensional polymer ions or charged particles. There is some evidence that a minor amount of cyclic tetramer ion may also be present.

Even in 1928, Harman (34) concluded from conductivity, transfer numbers, activity coefficients, hydrolysis, osmotic activity, freezing point data, phase relations, and diffusion experiments that there are only two simple silicates, Na_2SiO_3 and NaHSiO_3 , and that silicates in the $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio range of 2:1 to 4:1 become increasingly "colloidal."

Viscosity studies by Main (35) led to the conclusion that above a ratio of 2 $\text{SiO}_2 : 1$ Na_2O , colloidal aggregates of some type were present, along with simple silicate ions. Hägg (36) reached similar conclusions from potentiometric measurements.

Nauman and Debye (37) carried out light scattering studies on carefully filtered solutions of different $\text{SiO}_2 : \text{Na}_2\text{O}$ ratios and measured the following molecular weights (expressed as anhydrous SiO_2). They concluded that all ratios less than 2.0 there are no polymers or particles, but at higher ratios increasing amounts are present.

| Molar Ratio $\text{SiO}_2 : \text{Na}_2\text{O}$ | Average Mol. Wt. |
|-----------------------------------------------------|------------------|
| 0.48 | 60 |
| 1.01 | 70 |
| 2.03 | 150 |
| 3.32 | 325 |
| 3.9 | 400 |

In a potassium silicate solution of 3.8 molar ratio, Brady, Brown, and Huff (38a) found an average molecular weight of 2000.

Using ^{29}Si nmr, Marsman (38b) examined solutions of sodium potassium and tetraethylammonium silicate with molar ratios of base: Si of 4:1 to 0.02:1. The following species were detected: tetrafunctional branching groups, $\text{Si}(\text{OSi})_4$; trifunctional ($\text{HO})\text{Si}(\text{OSi})_3$; middle groups, $(\text{HO})_2\text{Si}(\text{OSi})_2$; end groups, $(\text{HO})_3\text{Si}(\text{OSi})$; and orthosilicate, $(\text{HO})_3\text{SiO}^-$. These are in equilibrium, and equilibrium constants were derived. With lower ratios of base to alkali, tetrafunctional groups predominate, indicating the presence of colloidal particles.

Engelhardt et al. (38c) reviewed similar studies reported up to 1975 and made more detailed measurements by which they identified different cyclic tetramers and double-ring trimer (a prism-like hexamer). Many types of ions are in equilibrium and as the ratio of Na:Si falls below 1.0 ($\text{SiO}_4:\text{Na}_2\text{O}$ over 2.0), branching and cross-linking groups begin to predominate. This is in agreement with other types of evidence that as the $\text{SiO}_4:\text{Na}_2\text{O}$ ratio exceeds 2:1, colloidal species begin to be present.

Infrared measurements can be used to identify simple silicate ions (absorption band at 950 cm^{-1}) and distinguish from polymeric species of molecular weight up to 10^6 (absorption at 1120 cm^{-1}) (39).

In similar studies, Borisov and Ryzhenko (40) observed the absorption and reflection spectra (500–1700 cm^{-1}) to vary with the $\text{SiO}_4:\text{Na}_2\text{O}$ ratio. In concentrated 1.5 ratio solution of $(\text{HO})_2\text{SiO}_4^{2-}$, and $(\text{HO})(\text{SiO}_4)\text{O}_4^{4-}$ the cyclic tetramer ion predominated, but disappeared when more alkali was added or when the solution was diluted. No dimer or trimer was mentioned.

Dilution with attendant depolymerization probably explains why Greenberg (41) concluded from a study of the literature and his own emf and conductance measurements that the data do not require postulating polymeric species even in solutions of 3 $\text{SiO}_4:\text{Na}_2\text{O}$ ratio. However, careful measurements at different concentrations gave valuable information as to the variation of pK_1 , the first ionization constant of Si(OH)_4^- to HSiO_3^- , at different ionic strengths, the value being 9.85 at zero ionic strength.

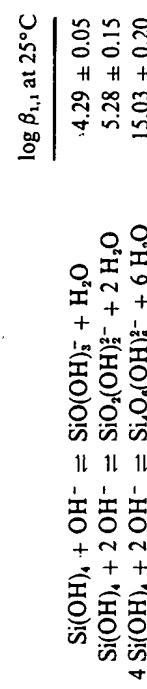
By chronopotentiometric and thermogravimetric methods, Franks and Mukherjee (42) identified in a 2.5 $\text{SiO}_4:\text{Na}_2\text{O}$ ratio melt the ions SiO_4^{4-} , $\text{Si}_2\text{O}_7^{6-}$, and $\text{Si}_3\text{O}_{10}^{8-}$ by their electroreduction potentials. However, there is no evidence that these ions retain their identity when the glass dissolves in water.

Using a technique developed by Sillén and co-workers, Lägerström (43) studied sodium silicate in 0.5 and 3.0 M solutions of sodium perchlorate to maintain constant ionic strength, measuring the emf values with a hydrogen electrode. For solutions corresponding to molar $\text{SiO}_4:\text{Na}_2\text{O}$ ratios of 2:1 to 2.8:1 (1–0.7 negative charges per Si atom), the data can be explained by assuming that three monomeric species, Si(OH)_4^- , $\text{Si}_2\text{O}_5(\text{OH})_3^-$, $\text{Si}_3\text{O}_9(\text{OH})_2^{2-}$, and the tetramer $\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$ were present. In 3 M NaClO_4 solution some additional ions, $\text{Si}_2\text{O}_5(\text{OH})_2^{2-}$, and $\text{Si}_3\text{O}_9(\text{OH})_4^{4-}$, were postulated. Different $\text{SiO}_4:\text{Na}_2\text{O}$ ratios were obtained by starting with various proportions of colloidal silicic acid, NaOH , HClO_4 , deaerated water, and NaClO_4 solution with special precautions to exclude CO_2 . Equilibrium constants were calculated for all species. As long as clear solutions (free from visible colloid) were involved, equilibria were attained rapidly.

In solutions where there were less than 0.75 negative charges per silicon atom ($\text{SiO}_4:\text{Na}_2\text{O} = 2.67:1$), the concentration of Si(OH)_4^- reached the approximate solubility of colloidal silica (120 ppm at 25°C and 216 at 50°C), and colloidal species were formed. Thus sodium silicates with ratios higher than 2.6 contained not only monomeric ion species and tetramer, but also higher polysilicates or very small colloidal particles bearing negative charges.

Ingri (44a) carried out a similar series of pH titrations in a 0.5 M NaCl solution with similar results, and also gave further support to the existence of the tetramer

$\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$. The following constants were reported:



Following Ingri, Busey and Mesmer (44b) extended potentiometric studies to 290°C in 1 M NaCl solutions at silica concentrations of 0.005–0.05 m. The equilibrium quotients for the ionization of $\text{Si}(\text{OH})_4$ to $\text{SiO}(\text{OH})_3^-$ and $\text{SiO}_2(\text{OH})_2^{2-}$ were determined in 0.1–5 m NaCl up to 300°C . In the more concentrated (0.02 m) solutions at around pH 8–10 some of the silica was present as the polyanion $\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$, but the amount of this form decreased at higher temperature.

A more detailed picture emerges from ultracentrifuge studies of sodium silicate in 0.5–2 M NaCl solutions, by Aveston (31). He studied solutions in which each silicon atom carried from 0.5 to 1.0 charges, corresponding to $\text{SiO}_2:\text{Na}_2\text{O}$ ratios of 2:1 to 4:1. The data suggest that although the cyclic tetramer may be an important component, there must exist a series of higher polymers in equilibrium, the average molecular weight increasing first gradually and then more rapidly as the $\text{SiO}_2:\text{Na}_2\text{O}$ ratio is increased from 2:1 to 4:1. Converting the "hydroxyl number" (charges per Si atom) to $\text{SiO}_2:\text{Na}_2\text{O}$ molar ratio, the following approximate average degrees of polymerization, hence average molecular weights, were found in 0.5 M NaCl solution. The molecular weight increased with the strength of the solution:

| Molar Ratio $\text{SiO}_2:\text{Na}_2\text{O}$ | Degree of Polymerization (as SiO_2) | Mol. Wt. (as SiO_2) |
|---------------------------------------------------|-----------------------------------------------------|----------------------------------|
| 2.0 | 2.5 | 150 |
| 2.2 | 3 | 180 |
| 2.6 | 7 | 420 |
| 3.1 | 15 | 900 |
| 4.0 (extrapolated) | 27 | 1600 |

In addition to monomers and tetramer, but no dimer or trimer, the polymers were assumed to consist of units containing q silicon atoms with p charges to which monomer and hydroxyl ions are added stepwise:

$$B_{p,q} = \frac{[\text{Si}_q(\text{OH})_p]^{q+1}}{[\text{Si}(\text{OH})_4]^q [\text{OH}^{-}]^p}$$

The authors did not assume any condensation of SiOH groups as polymerization progresses. However, the equation might be rewritten on the assumption that the particles contain anhydrous SiO_2 cores and a surface of $\text{Si}(\text{OH})_2$ with a certain portion of the hydroxyl groups ionized. Based on the maximum surface charge on larger

particles, about 40% of the SiOH groups on the surface are probably ionized. In this case, there would be a decreasing fraction of the total silica bearing negative charges, that is, the ratio of p/q would decrease with molecular weight once the degree of polymerization reached about 10–12, above which all silicon atoms cannot be on the surface of roughly spherical particles.

For $p = q = 1$:

$$\log \beta_{1,1} = \frac{[\text{Si(OH)}_6^-]}{[\text{Si(OH)}_4^-] [\text{OH}^-]} = 4.72$$

This value compares with 4.29 from Ingrī's data (44a).

Electrical conductivity measurements on potassium silicate of $\text{SiO}_2:\text{K}_2\text{O}$ molar ratios from 0.39 to 4.78 were made by Ivanov and Gur'eva (45). Anion mobilities were determined and interpreted on the basis of the usual assumption that $(\text{HO})_2\text{SiOSi(OH)}_2^{2-}$ and $(\text{HO})_3\text{SiO}^-$. Dissociation constants of the silicate ion in dilute sodium silicate solution from 0 to 250°C were calculated from conductivity measurements by Ryzenko (46).

The nature of silicate ions in molten $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (m.p. 32.38°C) was extensively studied by Thilo and associates, who used the lowering of the melting point to establish the number-average molecular weight of the silicate ions (47–49). The degree of hydrolysis depended on the $\text{SiO}_2:\text{Na}_2\text{O}$ ratio and not on concentration. At extreme dilutions the species Si(OH)_4 , $(\text{HO})_2\text{SiO}_2^{2-}$, and $(\text{HO})_3\text{SiO}^-$ are present. At higher concentrations equilibria set in between these monomers and higher molecular weight anions or particles.

At equilibrium, the average molecular weight of the silica varied inversely with Na_2O content (50).

Higher degrees of polymerization were visualized as occurring stepwise. This could, of course, also be interpreted as a change in particle size:



A general equation was developed and an equilibrium constant calculated for $\text{SiO}_2:\text{Na}_2\text{O}$ ratios from 2.0 to 3.34. However, the relation between these observations in molten Glauber's salt to the molecular weight distribution in water is not known.

Another approach by Thilo and associates (51) was to precipitate silicates from solution as the silver salts. Starting with $\text{SiO}_2:\text{Na}_2\text{O}$ ratios of 1 and 2, the degree of polymerization of silica in the silver salt varied inversely with the silica concentration and content of neutral salt. It was suggested that the silver salt, containing one silver atom per silicon atom, was a linear polymer, although no viscosity or molecular weight measurements were made.

Effects of Diluting Silicate Solutions

Since the concentration of hydroxyl ions and pH are reduced when concentrated alkali metal silicate solutions are greatly diluted, it is not surprising that hydrolysis

of silicate ions occurs and a large part of the silica is converted to higher polymeric species or colloid along with a residual silicate of lower $\text{SiO}_2:\text{Na}_2\text{O}$ ratio.

The electron microscope was used by McGarry and Hazel (52) to characterize the colloidal particles in 3.45 $\text{SiO}_2:1\text{ K}_2\text{O}$ potassium silicate solutions which had been diluted out from 10 to 0.03% SiO_2 in various ways. The samples were further diluted to 0.015% SiO_2 just before being examined. When diluted directly to 0.03%, 89% of the particles were from 1 to 5 nm in diameter. When diluted to 0.3% silica and aged for an hour and then diluted to 0.03%, the number-average diameter was 8 nm.

The results indicate that when the solution is aged at a concentration of 0.3% the 1–2 nm colloidal particles that were in the original 10% silicate act as nuclei upon which the monomeric silica, liberated by hydrolysis of silicate ions, is deposited. On the other hand, when the 10% solution is diluted directly to 0.03% SiO_2 , or 5×10^{-3} molar, the pH is 10.25 and all the silica passes into solution as Si(OH)_4 , and HSiO_3^- ions, and even the original 1–2 nm polysilicate ions or particles slowly dissolve. As seen in Chapter 1, at pH 10.26 the total solubility of silica including Si(OH)_4 and HSiO_3^- is around 0.05%. The authors used pencyanol chloride to detect the presence of colloid species. The dye micelles formed on the colloid by absorption shifted the color from blue to red (600 to 500 nm).

The further polymerization of the colloidal species owing to the lower pH when a 3.3 $\text{SiO}_2:\text{Na}_2\text{O}$ silicate solution is diluted was also studied by Lehman and Shuldener (53). They measured the amount of molybdate-reactive silica in solution over a period of days and found that at a concentration of about 0.14% SiO_2 , the amount of reactive silica, presumably monomeric species, decreased over a period of 2 days, although some further drop was noted over 1 week. The same occurred at 0.07% silica but not at 0.03%, where complete depolymerization occurred and all the silica was molybdate-reactive within a few hours.

When 3.25 ratio sodium silicate solution is diluted to around 2% SiO_2 and heated for 1 hr, there is disproportionation whereby colloidal particles grow in size, while the $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of the so-called crystalloidal or dialyzable soluble silicate approaches 2.6:1 or 2.0:1, depending on dilution. It is my experience that during this time the solution is supersaturated with respect to amorphous silica so that any clean surface of glass or metal oxide becomes coated with a film of silica to a thickness of a few nanometers.

Effect of Alkali Metal Salts and Other Coagulants

The addition of a salt of a polyvalent metal to a solution of a soluble silicate results in formation of a precipitate of a metal silicate. In this precipitate, silicate ions are presumably linked together by the metal ions to form an insoluble network. On the other hand, the addition of a salt of a monovalent metal, for example, sodium chloride, to a solution of sodium silicate yields a precipitate that will redissolve if the system is diluted with water.

The alkali metal silicate is salted out especially easily when the ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ is greater than 2:1. The fact that the precipitate can be dissolved in water suggests that it may consist of polysilicate ions linked together by coordina-

tion through sodium ions; such linkages would persist only in the presence of a large excess of sodium ions.

Further details of the effects of a sodium salt such as the chloride or sulfate on a solution of sodium silicate have been summarized by Vail (1). Thus sodium chloride causes separation of a precipitate of sodium silicate which is more siliceous than the original solution. In smaller amounts, sodium chloride and also the sulfate and carbonate increase the viscosity of sodium silicate solutions. It appears that the added sodium salt coagulates the colloidal or high molecular weight polysilicate ions but has less effect on the metasilicate ions.

The effect of salts on the equilibria in a silicate solution was studied by Pevzner et al. (54) up to a NaCl concentration of 5 N, with silicon concentrations of 0.001–0.3 g-ion l⁻¹ in the pH range 10.2–14.0. Equilibrium was approached from lower and higher pH. The dissociation constants (*pK*) for water at 25°C in 0.5, 3, and 5 N salt solutions are 13.7, 14.1, and 15.2, respectively. The tetrameric silicate ion was detected, as had also been reported by others (44). It is noteworthy that no dimer or trimer was mentioned. The data are summarized in Tables 2.3 and 2.4.

The effect of salt on the degree of polymerization of the polysilicate ions in aqueous potassium silicate was examined by Brady, Brown, and Huff (55), using the light-scattering method. The molar ratio of SiO₂:Na₂O was 3.8:1 and in freshly diluted solutions the weight-average molecular weight of the SiO₂ was about 2000. When neutral salts were added, the apparent molecular weight increased in proportion to the fourth power of the salt concentration and in inverse proportion to the square root of silica concentration. In alkaline solution, the molecular weight varied with the temperature. The salt-induced polymerization at high pH was reversible upon dilution, but the acid-induced polymerization at neutral or lower pH was irreversible.

It seems likely that at high salt concentrations the cations act as cross-links between polyions through coordination with polysilicate oxygen atoms which replace coordinated water on the cations. This would be reversed when water is added. On the other hand, acid-induced polymerization leads to formation of siloxane (Si-O-Si) bridges between the polysilicate ions which are not broken upon dilution.

Table 2.3. Composition and Stability of Silicate Ions at 25°C in 0.5, 3.0, and 5.0 M Aqueous Sodium Chloride Solution

| Equilibrium | Logarithm of the Equilibrium Constants in Solution with Ionic Strengths | | |
|---------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|------------|------------|
| | 0.5 | 2.0 | 5.0 |
| Si(OH) ₄ + OH ⁻ ⇌ Si(OH) ₃ ⁻ + H ₂ O | (1) 4.3 ± 0.1 | 4.6 ± 0.1 | 5.6 ± 0.2 |
| Si(OH) ₄ + 2 OH ⁻ ⇌ SiO ₄ (OH) ₂ ²⁻ + 2 H ₂ O | (2) 5.3 ± 0.2 | 6.0 ± 0.2 | 7.1 ± 0.2 |
| 4Si(OH) ₄ + 2 OH ⁻ ⇌ Si ₄ O ₁₀ (OH) ₈ ⁴⁻ + 6 H ₂ O | (3) 15.1 ± 0.3 | 11.0 ± 1.0 | 12.0 ± 1.0 |
| 4Si(OH) ₄ + 4 OH ⁻ ⇌ Si ₄ O ₁₀ (OH) ₄ ⁻ + 8 H ₂ O | (4) — | ~25 | ~27 |

Source. Data by Pevzner et al. (54).

Table 2.4. Changes in Free Energy, Enthalpy, and Entropy for the Formation of Silicate Ions in 5.0 M Aqueous Sodium Chloride Solutions at 25°C

| Equilibrium ^a | −ΔG (kcal g-ion ⁻¹) | −ΔH (kcal g-ion ⁻¹) | ΔS (eu) |
|--------------------------|---------------------------------|---------------------------------|---------|
| 1 | 7.6 ± 0.3 | 1.0 ± 0.5 | 22 ± 3 |
| 2 | 9.7 ± 0.3 | 1.5 ± 0.5 | 28 ± 3 |
| 3 | 16.4 ± 1.5 | 3 ± 1 | 45 ± 8 |

Source. Data by Pevzner et al. (54).

^a The types of equilibria are indicated by the numbers given in Table 2.3.

According to Prikhod'ko and Molchanov (56), the addition of alcohol or acetone to a solution of sodium metasilicate causes the formation of two liquid layers, the silicate accumulating in the lower layer. It seems probable that this is a simple dehydration of the silicate solution, the organic solvent removing water from the silicate solution and being immiscible because of the "salting-out" effect of the ions in the lower layer. Ordway (57) studied silicate of other ratios and concluded that organic solvents always precipitate a liquid or a solid phase containing a higher ratio of SiO₂:Na₂O than the original aqueous solution of silicate. This indicates that, whereas the silicate separates from a fluid layer rich in organic solvent, the sodium hydroxide is soluble in this organic layer and thus leaves a silica-rich aqueous phase.

Ammonium hydroxide is similar to alcohol in its effect. Sodium hydroxide is soluble in strong ammonium hydroxide or liquid ammonia, but sodium silicate is not; a process of purification of sodium hydroxide from small amounts of sodium silicate has been patented by Muskat and Ayres (58a) in which, at certain high concentrations of ammonia and water, the ammonia-rich layer dissolves the sodium hydroxide, while the sodium silicate in the system accumulates in an immiscible lower layer.

Effects of this type are apparently involved in a process for depositing silica coatings on glass from a solution of sodium silicate containing a critical amount of a "clustering" or "coacervating" agent such as NH₄OH, Na₂SO₄, or CH₃OH at ordinary temperature (58b).

Conversion to Silicic Acids

The nature of the silica in silicate ions in any alkaline solution cannot be determined by a chemical measurement that involves any change in the concentration of silica or alkali, electrolyte content, or temperature because these all shift the equilibrium between monomeric and various polymeric ion species. However, if a sample is simultaneously and instantaneously diluted and acidified to pH 2 at less than 30°C, the resulting silicic acid is sufficiently stable to permit characterization. The problem is to ensure that acidification is so sudden that the various silica species do not have time to polymerize or depolymerize as the pH is dropped from the usual region of

by converting the individual silicate ions directly to trimethylsilyl derivatives, which were identified after separation by thin-layer chromatography. This is possible if the derivatives are soluble, that is, if the silicate ion exists as isolated units and not as infinite chains or three-dimensional siloxane networks. Thus Wieker and Hoebbel (66) showed that when $\text{Li}_4\text{H}_2\text{SiO}_4$ solution is concentrated over H_2SO_4 , the ions are largely present as cyclic tetrasilicate. Also, crystalline $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ actually contains cyclohexasilicate ions and should be formulated $\text{Na}_4\text{Ca}_4(\text{Si}_6\text{O}_{18})$.

Similarly, these authors (75) converted the following silicates to the corresponding trimethylsilyl (T) derivatives which are used as standards for the identification of individual silicic acids:

| Crystal | Formula | Structure |
|--------------------------------------------------------------------------------------|-------------------------------------------------|--------------------|
| $\text{Na}_2\text{H}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$ | T ₄ SiO ₄ | Monomer |
| CaSiO_4 | T ₄ SiO ₄ | Monomer |
| $\text{Na}_6(\text{Si}_2\text{O}_7)$ | T ₆ Si ₂ O ₇ | Dimer |
| $\text{Na}_4\text{Cd}_2(\text{Si}_3\text{O}_10)$ | T ₆ Si ₃ O ₁₀ | Linear trimer |
| $\text{Si}_4\text{O}_3\text{Cl}_{10}$ | T ₁₀ Si ₃ O ₁₃ | Linear tetramer |
| $(\text{CaSiO}_3)_3$ | T ₆ Si ₃ O ₉ | Cyclic trimer |
| $(\text{KHSiO}_3)_4$ | T ₈ Si ₄ O ₁₂ | Cyclic tetramer |
| $[(\text{CH}_3)_3\text{N}^+]_{10}\text{Si}_7\text{O}_{19} \cdot x\text{H}_2\text{O}$ | T ₁₀ Si ₇ O ₁₉ | Tricyclic heptamer |
| $[(\text{CH}_3)_3\text{N}^+]_8\text{Si}_8\text{O}_{20} \cdot 6\text{H}_2\text{O}$ | T ₈ Si ₈ O ₂₀ | Cubic octamer |
| $[\text{Cu}(\text{en})_2]_4\text{Si}_8\text{O}_{20} \cdot 30\text{H}_2\text{O}$ | T ₈ Si ₈ O ₂₀ | Cubic octamer |

In this octamer, referred to as a "double-four-ring" structure there are eight silicon atoms at the corners of a cube.

Silicates with Coordination Numbers Four and Six

It has been previously theorized that in aqueous silicate solution silicon is coordinated with six oxygen atoms. Such views of Weyl (76) and Treadwell and Wieland (77) were discussed by Iller (78). However, more recent spectroscopic studies of silicate solutions seem to indicate that the *silica is 4-coordinated with oxygen* and that the $\text{Si}(\text{OH})_6^{2-}$ ion, for example, does not exist, at least in solution. Fortnum and Edwards (79) concluded that $\text{Si}(\text{OH})_6^{2-}$ was not present in solution because Raman lines analogous to those of SiF_4^{2-} , PF_6^- , and TeO_4^{2-} were not found. The four low intensity lines found at 448, 607, 777, and 935 cm^{-1} suggested that the ion is $(\text{HO})_2\text{SiO}_2^{2-}$ since it is similar to $(\text{HO})_2\text{PO}_4^{2-}$, which gives lines at 401, 511, 885, and 1050 cm^{-1} .

Similar conclusions were reached by Early et al. (80), who also noted the similarity of Raman spectra of $(\text{HO})_2\text{SiO}_2^{2-}$ and $(\text{HO})_2\text{SO}_4^{2-}$. Using H_2O and D_2O , Freund (81) examined silicate solutions with Raman-laser spectra and identified $(\text{HO})_3\text{SiO}^-$, $(\text{HO})_2\text{SiO}_2^{2-}$, and $(\text{HO})_3\text{SiO}_2^{2-}$, the latter only at very high alkali concentrations. Equilibrium was obtained rapidly and completely. There was no evidence for the presence of dimer species.

SOLUTIONS OF POLYSILICATES

For many years it was supposed that alkali silicate solutions with $\text{SiO}_2 : \text{M}_2\text{O}$ ratios higher than 4:1 could not be made. The corresponding glasses are not homogeneously soluble in water. Attempts to dissolve quartz or amorphous silica powders in a minimum of NaOH solution to achieve the desired higher ratios were not successful. Liquid silicates with ratios higher than 4:1 were sought for use in adhesives because the lower alkali content was anticipated to furnish bonds that are more water resistant. Also, in refractory compositions, lower alkali was needed to raise the softening point and improve refractory character.

As discussed at the beginning of this chapter, silicates with $\text{SiO}_2 : \text{Na}_2\text{O}$ ratios of 4:1 to about 25:1 are usually referred to as "polysilicates." They do not have the high content of sodium and silicate ions as do the conventional soluble silicates, which have ratios less than 4:1. However, they contain much more alkali than necessary to stabilize sols of smallest particle size manufactured and sold as colloids. The borderline between a polysilicate solution and an "alkali-stabilized sol of colloidal silica" can logically be drawn at the particle size of the silica below which the increased solubility of the silica as $\text{Si}(\text{OH})_4$ at ordinary temperature causes the

particles to grow spontaneously unless more alkali is added. However, when particles less than 5 nm in size are stabilized against growth by adjusting the ratio to less than 25:1, an increasing and substantial fraction of the silica is converted to silicate ions. Thus a "polysilicate" solution may be considered to be an equilibrium mixture of ionic and negatively charged particles of colloidal silica of such extremely small size that they can be classed also as polyanions.

Because lithium silicates are so different in behavior from sodium and potassium silicates, lithium polysilicate is discussed separately.

Sodium Polysilicate

The advantage of a binder having a $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio of 10:1, for example, is demonstrated by the fact that such mixtures of an alkali metal silicate and a colloidal silica sol are proposed for making waterproof fireproof coating mixtures even though the mixtures have a short shelf-life (88).

During the development of concentrated silica sols stabilized with NaOH around 1950, it was realized that the smaller the particle size, the more alkali and the lower the $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio required for stabilization. However, in the ratio range of about 4:1 to 25:1 the concentrated compositions were generally found to be unstable, and eventually gelled. When a 3.25 ratio sodium silicate solution was added to a concentrated silica sol to reduce the $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio from 100:1 to 5:1, for example, a gel immediately formed. However, Iler (89) found that by aging or warming the mixture, a stable liquid was again obtained. Thus solutions with ratios from 4.2:1 to 6:1 containing 10–30% SiO_2 could be prepared from sols originally containing typically 5–25 nm particles. However, longer heating destabilizes the mixture and an insoluble crystalline polysilicate or gel appears. The polysilicate solution is a clear, transparent fluid of low viscosity in which around half of the silica is present as soluble or ionic silicate, as shown by its reactivity with the molybdic acid reagent. Thus much of the silica that was introduced as colloid remains as such, but the particle size is smaller owing to some depolymerization at equilibrium.

The unique nature of the product is shown by the fact that when it is mixed with a silica sol containing an equal weight of 7 nm colloidal silica along with a sol containing an equal weight of colloidal silica as 100 nm particles, there is formed a mixture which, when cast as a film on glass, dries at 150°C to a clear, hard, adherent, water-resistant coating. The spaces between these by the still smaller colloidal component of the polysilicate and, in turn, the remaining spaces of molecular size by the soluble ionic silicate species. Once dried, the sodium apparently is adsorbed on the extensive silica surface so that no soluble silica remains and the film is impervious.

Instead of starting with a sol of preformed particles, Oken (90) claimed that by starting with a low molecular weight solution of silicic acid, temporarily stable liquids could be obtained with $\text{SiO}_2 : \text{Na}_2\text{O}$ ratios in the range 4:1 to 6:1, as in Iler's composition, and also from 8:1 to 40:1.

More recently, compositions with ratios higher than 4:1 have been prepared by heating an amorphous silica powder with 3.22 ratio sodium silicate to above 100°C

to cause intumescence, and then the partly dried mass is further heated to 315°C, after which the mass can be dissolved to give a polysilicate solution (91). The higher temperature apparently partly dissolves the agglomerated silica powder, bringing about its disaggregation. Probably the amorphous powder employed must consist of ultimate silica particles of the same size range as in the sols employed in earlier processes. According to a German patent, if waste silicic acid powder from the AlF_3 process is used, it is so lightly agglomerated that it can be dispersed by alkali alone to give a solution of 4.3:1 ratio of $\text{SiO}_2 : \text{Na}_2\text{O}$ containing 13.7% SiO_2 (92).

Potassium Polysilicate

It has not generally been recognized that in the polysilicate system, the potassium ion behaves very differently from sodium. Although the coagulating effect of these ions is generally similar in most colloid systems and even in colloidal silica at pH 7–10, the potassium loses its coagulating effect at higher pH but sodium does not. (This is discussed in further detail in Chapter 4.)

When concentrated 3.25 ratio sodium silicate is mixed with an alkali-stabilized sol containing 30% silica, coagulation and gelling occur at once, but they do not occur if potassium silicate is added. This is apparently the basis for the disclosure of Wittersdorf (93). Thus stable mixtures of colloidal silica and potassium silicate can be prepared with a silica concentration of 15–30 wt. %, with $\text{SiO}_2 : \text{K}_2\text{O}$ molar ratios of 11:1 to 24:1. Although it is not so stated, such compositions are relatively stable toward prolonged heating in comparison with similar sodium based mixtures, which tend to crystallize.

Appreciation of this effect has led to the development of a number of practical applications. Thus amorphous silicic acid powder is heated with 2.4:1 ratio potassium silicate solution to give a viscous solution that forms a binder for a pigmented coating on asbestos-cement board (94). The final molar ratio of $\text{SiO}_2 : \text{K}_2\text{O}$ is 5.7:1. A composition with similar use is described by Yano (95).

Another unusual application of the compatibility of potassium silicate with sodium-free colloidal silica is described by Shoup (96). By mixing concentrated potassium silicate solution with a concentrated silica sol and adding an ester, aldehyde, or amide which liberates acid as a homogeneous gelling agent, very strong, dense, uniform silica gels can be made in cast shapes. When washed with acid to remove the potassium salt, these gels are so strong and coherent that they dry in the shape in which they are cast. Because the silica is so concentrated, cracking is minimized as the gel shrinks as it is dried. When fired at 900°C it gives a strong body with 70% by volume porosity. It can then be fired at 1400°C and further shrunk to an object of clear fused silica without losing its relative shape (97).

LITHIUM SILICATES

The lithium ion is very different from sodium or potassium in its behavior in silica systems. The lithium ion resembles these elements to some extent at ordinary

temperature but above about 60°C it assumes some of the characteristics of calcium. Thus, although a solution of lithium silicate can be made by dissolving amorphous silica in LiOH solution at 20–40°C, the silicate comes out of solution when heated. The effect is reversible; it is remarkable to see the solution solidify to a white mass when hot, then reliquify to a clear homogeneous state after being cooled to 25°C for a few hours.

Ordway (57) in 1907 studied the properties of lithium silicate with molar ratios of $\text{SiO}_2:\text{Li}_2\text{O}$ of 1:1 to 2:3:1 and noted the peculiar reversible insolubility when the solution was heated and cooled. Even as late as 1952, Vail (1) stated that the possible concentrations and ranges of composition of lithium silicate were much more restricted than in the case of sodium. In 1969, Wellems and Lange summarized the properties of available aqueous lithium silicate systems (19).

It is apparently only since 1950 that it has been appreciated that stable solutions of lithium silicates and polysilicates could be prepared with any desired $\text{SiO}_2:\text{Li}_2\text{O}$ ratio and that these have useful properties.

The difference from sodium is especially apparent in concentrated solutions with molar ratios of $\text{SiO}_2:\text{Li}_2\text{O}$ from 4:1 to 15:1 or higher. These are clear and quite stable at 25°C whereas, as previously discussed, most of the analogous sodium silicate compositions either gel or crystallize. Furthermore, the properties of concentrated sols of colloidal silica are appreciably different from those stabilized by sodium base, especially in regard to much greater compatibility with water-miscible organic solvents.

Lithium silicate solution cannot be made by dissolving the glass, so is prepared by dissolving very finely divided amorphous silica in LiOH solution at 20–50°C. However, the reaction apparently proceeds more rapidly at 75–250°C in an autoclave, whereby one obtains a solution of LiSiO_3 , plus a precipitate of higher ratio silicates which dissolves when the solution is aged at 20–30°C (98). A solution of 3.8 molar ratio can be prepared by adding 200 mesh silicon powder to a stirred 12% solution of $\text{LiOH}\cdot\text{H}_2\text{O}$, from which hydrogen is evolved, while the temperature is held at 38–45°C. The slightly viscous filtered solution contained 19% SiO_2 (99). Another approach is to prepare a cation-exchange resin in lithium form and pass a solution of sodium silicate through it to exchange sodium for lithium (100).

Commercial solutions of lithium polysilicate are reported with the following properties (102).

| | Poly silicate | Type 48 | Type 85 |
|------------------------------------------------|---------------|---------|---------|
| SiO_2 (%) | 20 | 20 | 20 |
| Li_2O (%) | 2.1 | 1.2 | 1.2 |
| Molar ratio $\text{SiO}_2:\text{Li}_2\text{O}$ | 4.8:1 | 8.5:1 | 8.5:1 |
| Viscosity (cps) | 12 | 8 | 8 |
| Specific gravity | 1.17 | 1.17 | 1.17 |
| pH | 11 | 11 | 11 |
| Shelf-life at 75°F (months) | 12 | 12 | 12 |

Since compositions of all $\text{SiO}_2:\text{Li}_2\text{O}$ ratios from 4:1 to 25:1 are soluble and stable, this system offered Iler an opportunity to examine the relation between the silica to alkali ratio and the nature of the colloid species present. Lithium polysilicate solutions were made by mixing solutions of polysilicic acid, obtained by ion exchange from 3:25 ratio sodium silicate, and lithium hydroxide and aging the mixtures at 25°C for a week until clear liquids were obtained at equilibrium. The solutions contained 10% of SiO_2 and the $\text{SiO}_2:\text{Li}_2\text{O}$ ratios ranged from 3:1 to 10:1. These solutions were compared by measuring the rate of formation of the yellow silicomolybdic acid when microsamples were suddenly mixed with molybdic acid solution at low pH. For each sample, the percent of the total silica, P , which had reacted at time t was noted at 2.5, 5, 10, 15, and 20 min at 25°C. A solution of sodium silicate of 3.3:1.0 M ratio was also included and found to react in about the same way as the lithium silicate solution of corresponding ratio.

It was assumed that the solutions all consisted, for the most part, of monomeric silicate ions and higher molecular weight polysilicate ions in the form of very small charged colloidal particles. Since the monomeric ions react with molybdate in about 2.5 min, the percent of monomeric silica, P_m , was noted in each case.

Then $P - P_m$, or p , was the percent silica in the polymeric state that had reacted at time t . This was found to follow the equation

$$\log \frac{100 - p}{100} = kt \quad (\text{see Figure 2.4})$$

The values of k , the relative reaction rate, were plotted against $(R - 2)^{-1}$ since colloidal species are present only at a ratio greater than 2:1. This gave the relation shown in Figure 2.5. Since, as has been elsewhere noted, the reaction rate is an inverse function of particle size of the colloid, it is concluded that the size of the colloid species must increase regularly and spontaneously in proportion to the degree to which the ratio exceeds about 2:1. This is at least true in the ratio range 3:1 to 10:1. At higher ratios, the particle size is less closely related to ratio, since it is well

Lithium Polysilicates

In 1954 it was discovered by Iler (101) that concentrated stable solutions containing $\text{SiO}_2:\text{Li}_2\text{O}$ molar ratios from 4:1 to 25:1 could be obtained by adding LiOH to a solution of polysilicic acid, to a suspension of silica gel, or to a silica sol free from alkali metal or other cations. Since the mixtures thickened or immediately set to a gel, this approach appeared useless until it was found that after a few hours or a day or so at ordinary temperature, the mass spontaneously liquefied. When such mixtures were heated to 80–100°C to accelerate liquefaction, they remained gelled. The liquid compositions contained both ionic and colloidal silica.

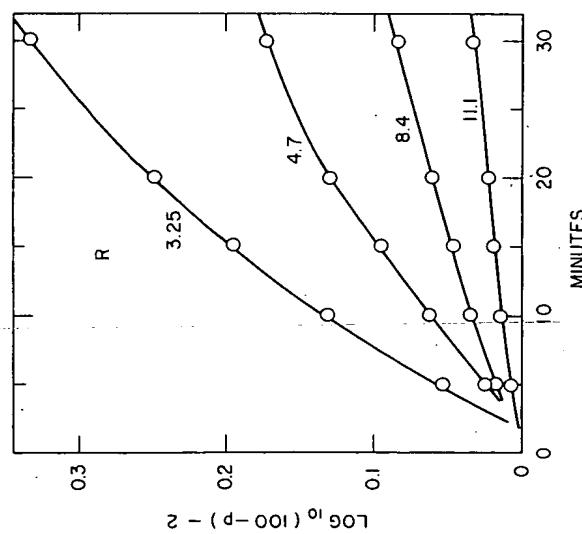


Figure 2.4. Reaction of colloid species of silica in lithium polysilicate solutions of different ratios of $\text{SiO}_2:\text{Li}_2\text{O}$ (indicated on curves) with molybdic acid reagent.

known that at ratios higher than 25:1, sols of different particle sizes can be stabilized at the same ratio without much, if any, difference in particle size.

Thus the polysilicate solution spontaneously equilibrates to a mixture of monomeric species and colloidal species, the size of which increases with increasing ratio over 2:1.

Numerous procedures for manufacture have been suggested. Cuneo (103) prepared a lithium polysilicate from a 2.6% silica sol obtained from sodium silicate by ion exchange, by adding LiOH to attain ratios of 2.5:1 to 8:1 and then concentrating the solution by vacuum evaporation to a silica content of 21%. More "crystalloidal," as opposed to colloidal, silica was said to be present because of the nature of the starting sol which probably contained silica particles 1-2 nm in diameter.

A lithium polysilicate solution of 3.5 M ratio can also be made by heating finely divided amorphous silica with LiOH solution at a molar ratio of 1.5:1, separating the precipitate that forms at elevated temperature, and letting it cool, whereupon it liquefies to a polysilicate solution containing 23.4% SiO_2 . Apparently the silicate that separates from hot solution is of higher ratio than that which remains (104). According to Patton and Cox (105), lithium silicates of molar ratios from 2:1 to 6.3:1 can be made in a similar manner at 75-150°C by leaving the precipitate in suspension and cooling to effect total solution. The polysilicate can also be made by dissolving silicon powder in LiOH solution at 50-80°C with $\text{Cu}(\text{OH})_2$ present as a catalyst (106).

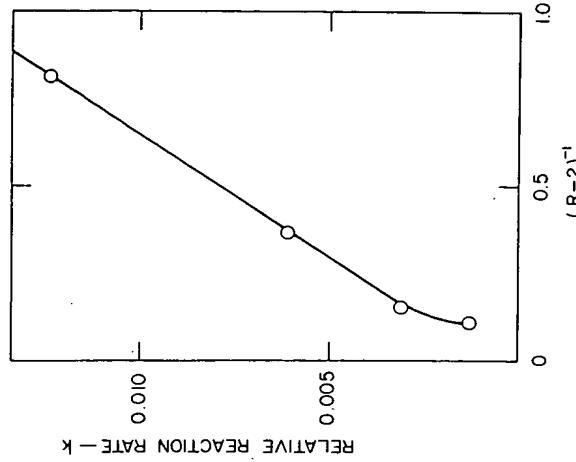


Figure 2.5. Relative rates of reaction of colloid species in lithium polysilicates with molybdic acid reagent versus $(\text{R} - 2)^{-1}$, where R is the molar ratio of $\text{SiO}_2:\text{Li}_2\text{O}$.

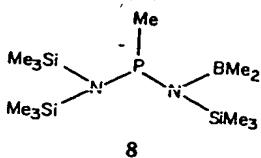
The presence of some lithium silicate in sodium or potassium silicate solutions is apparently of some advantage (107, 108).

Uses for Lithium Silicates and Polysilicates

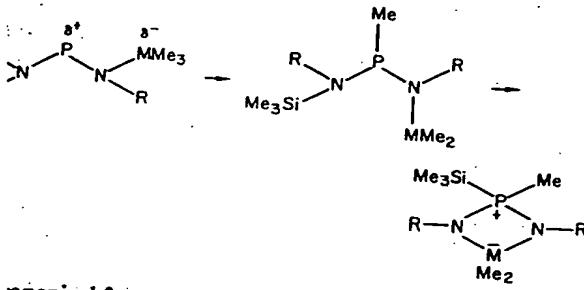
A major use of polysilicates is in anti-corrosion coatings containing finely divided zinc, where the silica acts as an inorganic binder (109, 110). The addition of an organosiliconate improves the water resistance of the coating (111). A similar composition is said to provide a binder for brake linings (112). For a similar reason, a minor amount of a styrene-acrylic copolymer emulsion may be added, which also gives improved adhesion to steel (113). Another additive to improve saltwater resistance is a small percentage of barium hydroxide (114). Barium silicate is more soluble than the calcium or strontium salt and liberates enough silicate ion into solution to inhibit the corrosion of aluminum by alkali, according to Dupre and Boorman (115). The adhesion and weldability of zinc-rich primers bonded with lithium polysilicate were improved by substituting some di-iron phosphide or cadmium for some of the zinc (116).

Some of the difficulties involved in using zinc-rich paints bonded with polysilicates were reviewed by Wright (117), who pointed out that in storage, slow reaction of zinc with the vehicle on aging reduced the quality of the final coating. Several types of soluble silicates were evaluated, but a lithium polysilicate with

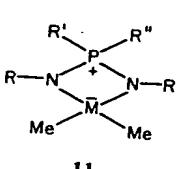
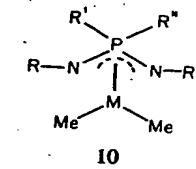
enfield from that of 9 and in the region expected for di-alkylphosphines.^{10,11} The ¹H NMR of 8 (Figure 2) consists of four resonances assignable as follows: PMe (d, 3 H, δ 1.60, J_{PNC} = 11.3 Hz), BMe (d, 6 H, δ 0.63, J_{PNC} = 1.2 Hz), NSiMe₃ (d, 9 H, δ 0.31, J_{PNSiCH} = 1.2 Hz), and N(SiMe₃)₂ (d, 1 H, δ 0.30, J_{PNSiCH} = 1.5 Hz). The separation between the two Me resonances remains constant at 1.5 Hz when the spectrometer frequency is increased from 90 to 200 MHz, thus indicating the Me doublet is due to coupling with the phosphorus. It is clear in 8 all Me₃Si groups are attached to nitrogen. This fact is confirmed by the ¹³C(¹H), (Me₃Si) spectrum of 8 which also shows no indication of a PSiMe₃ moiety. PMe (d, δ 25.6, J_{PC} = 3 Hz), BMe (br, δ 12–20.0), N(SiMe₃)₂ (d, δ 5.64, J_{PNSiC} = 1 Hz), and BNSiMe₃ (d, δ 5.34, J_{PNSiC} = 4.0 Hz). The 70-eV spectrum of 8 exhibits no molecular ion; the 100% peak is at m/e 279, which corresponds to loss of NBMe₂. The foregoing indicate that the structure of 8 is



On the isolation of 8 suggests that the most likely reaction may leading to the cyclic compounds 5, 6, and 9 is



Analogous forms, 10 and 11, can be written for the cyclic analogs 5, 6, and 9.



neutral (RN)₂PR' ligand behaves in a trihapto manner on Me₂M moiety,¹² while 11 implies formation of a via electron transfer from P to M. The ³¹P chemical shifts, 6, and 9 fall in the range of 30–60 observed for no, alkyl-substituted phosphonium cations,¹³ thus insinuating considerable zwitterionic character. The possibility that ligands can coordinate to transition metals is under investigation.

Acknowledgment. Generous financial support from the National Endowment (Grant CHE-7910155) and the Robert A. Dugdale, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Top. *Phosphorus Chem.* 1967, 5, 227–457 and references

coieties are known to coordinate in a trihapto manner to cyclohexamethylenecyclopentadiene rings. See: Schonberg, P. R.; Ampana, C. F. *J. Am. Chem. Soc.* 1979, 100, 7726–7728. Example: [Me₂P(NH₂)(NMe₂)]Cl (+39),¹¹ [MeP(NMe₂)₂]Cl (+62).¹¹

Nature of Species Present in an Aqueous Solution of Potassium Silicate

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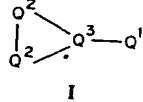
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We wish to report definitive evidence for the structures of 11 species present in an aqueous solution of potassium silicate. These include five ions which involve a ring containing three siloxy units.

Aqueous silicate solutions are important in the detergent industry¹ and geochemistry² and have some biochemical significance.³ Stable solutions of moderate concentration can only be achieved at high pH. Although these solutions might appear to be simple, in practice they are complex because the orthosilicate ion polymerizes in such a fashion as to yield a variety of species in dynamic equilibrium. Until recently, information about the nature of these species was obtained only indirectly, for instance, by trimethylsilylation followed by chromatographic separation.⁴ ²⁹Si NMR has given promise of more direct information,^{5–9} since a variety of peaks can be resolved in the spectra, but unfortunately there has been no clear way of assigning the peaks to given structures. Rapid proton exchange ensures that no (Si,H) coupling can be observed, and the natural abundance of ²⁹Si (4.7%) means that (Si,Si) coupling is also absent. Limited progress has, however, been achieved, and bands due to the monomeric orthosilicate species (Q⁰), end groups (Q¹), middle groups (Q²), and branching positions (Q³) have been recognized.^{5,6} Two further bands are the subject of dispute but have been tentatively assigned to Q² and Q³ units in three-membered rings.⁷ The Q designation refers to silicon bonded to four oxygen atoms, and the superscript number indicates how many of these bonds are part of siloxy bridges. Assignments of individual lines have been very sparse, only the monomer (Q⁰) and dimer (Q¹Q¹) peaks being recognized definitively.⁸ [The designations n-mer and n-membered ring refer to the condensed species containing n siloxy (SiO) groups plus the appropriate number of additional oxygen atoms. Throughout this discussion the states of protonation of the species present are ignored.] A third peak has been assigned to the cyclic trimer (Q³), and Harris and Newman⁷ have also tentatively assigned peaks to the linear trimer (Q¹Q²Q¹), the linear tetramer (Q¹Q²Q²Q¹), and a substituted cyclic trimer (I). Recently, we have begun



studies by using material enriched in ²⁹Si and have obtained some information from splitting patterns.⁸ In particular, five peaks were found to be unsplit, including those assigned as Q⁰, Q¹, and Q². Moreover, splitting evidence tended to confirm the existence of I but fell short of clear proof. Since the chemical likelihood of

- (1) Barby, D.; Griffiths, T.; Jaques, A.; Pawson, D. "Soluble Silicates and Their Derivatives" In "The Modern Inorganic Chemicals Industry", Thompson, R., Ed.; Chemical Society: London, 1977.
- (2) Vail, J. G.; Wills, J. H. *ACS Monogr.* 1952, No. 116.
- (3) Birchall, J. *New Trends Bio-Inorganic Chem.* 1978, 209.
- (4) (a) Dent-Glasser, L. S.; Lachowski, E. E. *J. Chem. Soc., Dalton Trans.* 1980, 393–398. (b) Dent-Glasser, L. S.; Lachowski, E. E.; Cameron, G. G., *J. Appl. Chem. Biotechnol.* 1977, 27, 39–47.
- (5) Engelhardt, G.; Jancke, H.; Hoebbel, D.; Wicker, W. Z. *Chem.* 1974, 14, 109–110.
- (6) Marsmann, H. C. *Z. Naturforsch. B* 1974, 29B, 495–499.
- (7) Harris, R. K.; Newman, R. H. *J. Chem. Soc., Faraday Trans. 2* 1977, 73, 1204–1215.
- (8) Harris, R. K.; Jones, J.; Knight, C. T. G.; Pawson, D. *J. Mol. Struct.* 1980, 69, 95–103.
- (9) Engelhardt, G.; Zeigan, D.; Jancke, H.; Hoebbel, D.; Wicker, W. Z. *Anorg. Allg. Chem.* 1975, 418, 17–28.

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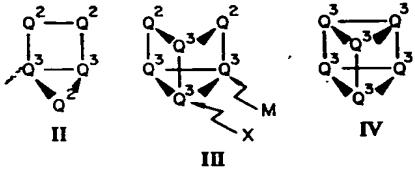
Table I. ^{29}Si NMR Chemical Shifts of Silicate Species^a

| system $\Delta\delta$ | Q^1Q^1 -8.620 | Q^2_3 -10.186 | Q^2_4 -16.096 | Q^2_6 -17.210 | Q^2_8 -25.580 | | | |
|-------------------------------------|---------------------------------------------|---------------------------------------------|-------------------------------------------------|-------------------------------------------------|--------------------------------|---------------------------------|-------------------------------|-------------------------------|
| system group $\Delta\delta^b$ | I Q^1 -8.072 | I Q^2_3 -9.870 | I Q^3_4 -18.234 | II Q^2 -16.355 | II Q^2_3 -9.863 | II Q^3_4 -17.160 | | |
| system group $\Delta\delta^b$ | III ^d Q^2 -16.048 | III ^d Q^3 -24.714 | III ^d Q^3 (M) -17.436 | III ^d Q^3 (X) -16.650 | V Q^2 -14.222 | V Q^3 -21.938 | VI Q^2 -14.511 | VI Q^3 -21.004 |

^a Present in the aqueous solution described in the text. ^b $\Delta\delta$ is the shift from the resonance of the monomer Q^0 , by using the high-frequency-positive convention. The monomer resonance is at δ -7.1 from TMS. ^c In a three-membered ring. ^d For the labeling M and X, see the molecular structure III.

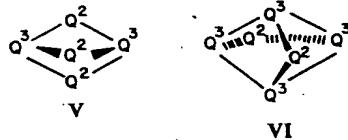
systems involving three-membered rings has been questioned, this situation is unsatisfactory.

The difficulties in the way of more definitive work have been (a) the complexity of spectra, which show that many species are present over a wide range of pH and concentration, (b) the low S/N and poor dispersion provided by first-generation Fourier transform NMR spectrometers, and (c) the lack of evidence linking peaks due to the same species. We have, therefore, decided to make use of two further techniques which are well-known in other areas of NMR but have not, to our knowledge, been hitherto employed for ^{29}Si , in addition to the concept of ^{29}Si enrichment. These techniques are (a) use of a very high-field spectrometer system (operating at ca. 100 MHz for ^{29}Si) and (b) ($^{29}\text{Si}, ^{29}\text{Si}$) homonuclear decoupling. Splitting patterns have provided essential additional evidence for particular species, and we have been able to definitively confirm the existence of I, which shows a first-order AMX_2 pattern for the per ^{29}Si isotopomer. This assignment also allows us to be reasonably certain of the existence of the cyclic trimer. Spectral analysis and homonuclear decoupling also show the existence of two other species involving the three-membered ring, viz., II and III, which give $(\text{AM})_2\text{X}$ and $(\text{AM})_2\text{RX}$ spin



systems, respectively. Moreover, the chemical shifts of the latter make it reasonably certain that one of the unsplit peaks (the singlet Y mentioned in our previous work)⁸ is due to the cage structure IV (double three-membered ring Q^3_6).

It proved to be possible to recognize and assign the splitting patterns due to two further species, V and VI, which have not been



postulated previously. The former gives a first-order A_3X_2 pattern and the latter forms an $(\text{AX}_2)_2$ spin system. The spectra of V and VI are illustrated in Figure 1. These two species give chemical shifts clear of the previously recognized bands. The Q^2 groups of V are responsible for the triplet (designated W) observed⁸ in our earlier study with ^{29}Si -enriched material.

Two further possible assignments may be made. The singlet X observed in our earlier work⁸ is probably the cyclic tetramer Q^2_4 . Finally, a sixth singlet, seen for the first time in the present work, may be tentatively assigned to the "cubic" cage compound (i.e., double four-membered ring), Q^3_8 , on the grounds that it has been previously postulated to exist in solution⁹ (the corresponding trimethylsilylated species certainly does),¹⁰ the chemical shift is

(10) Dent-Glasser, L. S.; Harris, R. K.; Jones, J.; Lachowski, E. E. *J. Mol. Struct.* 1979, 51, 239-245.

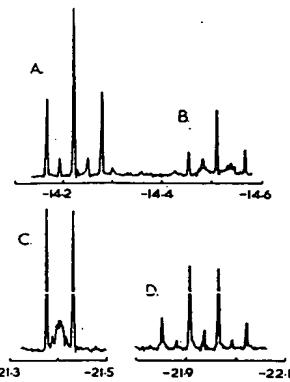
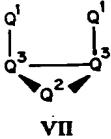


Figure 1. ^{29}Si NMR spectra of the silicate species V and VI (see the text) fully enriched in ^{29}Si . (A) Q^2 units of V, (B) Q^2 units of VI, (C) Q^3 units of VI, and (D) Q^3 units of V. The small peaks in A and D are due to species with one ^{29}Si replacing ^{28}Si . The frequency scale is in ppm with respect to the peak for Q^0 .

reasonable, and there are few other remaining structures that could be responsible for a singlet for the ^{29}Si -enriched situation.

Thus we have evidence for 11 separate species; our confidence in the structures range from ca. 70% to 100%. Apart from the monomer and dimer, these involve cyclic or cage compounds. Five species include three-membered rings, which therefore (contrary to expectation) must be particularly stable under the high pH conditions used. The remaining three species (as well as II, III, and IV) involve four-membered rings. The structures V and VI are clearly related. It is of interest that no species VII could be detected—presumably cyclization of the cis isomer to II occurs readily.



All this work has been carried out for a particular solution of KOH/SiO₂, which was 0.65 M in Si, with a ratio K:Si = 1:1. The solution was prepared by dissolving SiO₂, enriched to the 95.3% level and obtained from the Electromagnetic Separation Group, A.E.R.E., Harwell, in a medium consisting of KOH, H₂O, and D₂O. The spectrum shows a number of additional peaks for which assignment is not yet possible. The chemical shifts for the assigned species are given in Table I. The spectral analysis has assumed that only two-bond (Si, Si) coupling constants are large enough to be resolved. The way is now open for exploiting the techniques described here by the study of solutions with a variety of pH's and concentrations. We shall report fully on such work later.

The spectra were obtained at 298 K by using a Bruker WM-500 spectrometer with a 10-mm multinuclear probe head, operating at 99.36 MHz for ^{29}Si . Homonuclear decoupling was achieved by gating a synthesizer frequency source (which can be set in 1-Hz steps) synchronously with the A-D converter dwell clock, amplifying it to ca. 2 W, and coupling it to the observe coil of the probehead via a directional coupler with ca. 25 dB loss at 99 MHz.

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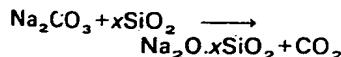
Sodium silicates

L S Dent Glasser

Commercial sodium silicates are produced from sand and either soda ash or caustic soda. Because these ingredients are so familiar, it comes as a slight shock to many people to discover that the products still present something of an enigma in their structures and properties. However, it is no surprise to discover that they are relatively cheap which, combined with a wide variety of applications, accounts for their great industrial importance.

Sodium silicates are manufactured as glasses, solutions, crystalline solids or soluble amorphous powders. About 3 Mt of these materials and derived products are produced annually. Although this is less than the production of chemicals such as sulphuric acid, ammonia or caustic soda, sodium silicates still rank as a major inorganic chemical product. Table 1 summarises some of the uses of sodium silicates in the US and UK. In the US roughly one third of the sodium silicate produced is consumed directly in the detergent industry, about half of this as an additive to washing powders. About another third serves as a source of silica for derived products such as silica gels and sols, alumina-silica cracking catalysts, zeolites, and precipitated silicas (widely used as carriers and filters). The remaining third is consumed in miscellaneous applications such as adhesives and cements, deflocculants, foundry applications, and vehicles in organic paints. The UK pattern is similar, except that rather more (about half) is used as a silica source for the chemical industry, and proportionately less in the other two major divisions.

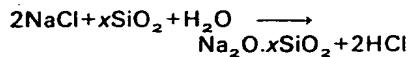
Most sodium silicate is produced via the furnace route, in which sodium carbonate and sand react at ca 1500 °C to give sodium silicate glasses of various compositions:



where $\text{Na}_2\text{O} \cdot x\text{SiO}_2$ represents the oxide ratio of the glass produced. Commercial solutions are produced from the glass by dissolving it in water under pressure.

The value of x specifies the mole ratio of the glass; this is virtually the same as the weight ratio, since the formula weights of Na_2O and SiO_2 are very similar (62 and 60 respectively). Most of the glass manufactured in the UK has weight ratio either of 2 ('alkaline glass') or 3.3 ('neutral glass'). However, silicates are so strongly basic (orthosilicic acid, H_4SiO_4 , has a pK_1 of about 9.4) that even solutions of the 'neutral' glass have pH values of 11 or more.

The furnace route is very wasteful of energy, and where sodium hydroxide is cheap, the alternative route—direct dissolution of sand in caustic soda solution—is attractive. This method however has the serious limitation that only lower ratio products, below about 2.5, can so far be produced by it economically. Moreover, handling caustic solution at the elevated temperatures and pressures needed poses real engineering problems. Direct reaction of NaCl , SiO_2 and H_2O :



using the volatility of HCl to pull the reaction to the right, looks even more attractive, but has not so far proved economic.

An excellent and authoritative review of soluble silicates and their derivatives appeared relatively recently^a and should be consulted for more detailed technical background and a very full list of references up to 1977. The main purpose of this article is to review current progress

Table 1. Uses of sodium silicates.

| Application | Percentage of US market ^a | Percentage of UK market ^b |
|-------------------------------------|--------------------------------------|--------------------------------------|
| Detergents | 30 | 24 |
| Silica source for chemical industry | 37 | 49 |
| Silicate based pigments | 20 | |
| Cracking catalysts | 10 | |
| Silica gels and sols | 4 | 45 |
| Zeolites | 1 | |
| Calcium silicates | 1 | |
| Metasilicates | — | |
| Titania pigments | 1 | 4 |
| Other | 33 | 27 |
| Adhesives | 4 | 4 |
| Cements | 4 | 7 |
| Roofing granules | 3 | |
| Building materials | | 2 |
| Ore flotation | 2 | |
| Water treatment | 2 | 1 |
| Textile bleaching | 2 | |
| Foundry binders | 1 | 11 |
| Welding rods | 1 | 1 |
| Miscellaneous | 15 | 1 |

^a PQ estimates from Schweiker, *J. Am. Oil Chem. Soc.*, 1978, 55, 36.

^b Estimates for 1979.

in the field, and only references not given in ref 1 are included.

Solid phases

The compositions of sodium silicates are conveniently displayed on a ternary diagram as in Fig. 1, which shows crystalline phases and the compositions of technical products. The crystal structures of the so-called metasilicate hydrates, $\text{Na}_2\text{SiO}_3 \cdot x\text{H}_2\text{O}$, have been known for some years: all in fact contain $\text{H}_4\text{SiO}_4^{2-}$ ions and should consequently be written $\text{Na}_2\text{H}_2\text{SiO}_4 \cdot x - 1\text{H}_2\text{O}$. They should properly be called 'dihydrogen orthosilicates' (cf phosphates), but the use of 'metasilicate' is enshrined in the technical literature, and workers in the field have mostly learned to live with it. Crystal structure determinations of $\text{Na}_3\text{HSiO}_4 \cdot 5\text{H}_2\text{O}$ and, more recently, $\text{Na}_3\text{HSiO}_4 \cdot 2\text{H}_2\text{O}$, show that these too contains orthosilicate groups.² ←

Phase relations on the alkaline side of the triangle are fairly well established, equilibrium being approached quite rapidly. However, the more remote the composition becomes from the $\text{Na}_2\text{C}-\text{H}_2\text{O}$ side of the diagram, the more one becomes entangled with metastable systems and the less easy it is to establish the true facts.

A number of relatively siliceous crystalline phases exist, four of which (magadiite, maketite, kenyaita and kanemite) have been found as natural minerals associated with soda lakes; several other compounds have been synthesised in the laboratory. Well established compositions are indicated in Fig. 1. Only one structure (maketite³) has been determined, and even the composition of many of these phases is still in doubt, as are the relationships between them. However it seems likely that a number of them are layer structures based either on single silicate sheets, of composition $\text{Si}_2\text{O}_5^{2-}$, like those found in maketite, or more complicated multiple sheets, perhaps similar to those described for $\text{Na}_2\text{Si}_3\text{O}_7$. They behave rather like clay minerals, many exhibiting variable basal spacings according to the degree of hydration and considerable ion-exchange capacity, in particular exchanging Na^+ for H^+ , so that compounds close to $\text{H}_2\text{Si}_2\text{O}_5$ and other condensed 'silicic acids' can be made.

Species in solution

The structure and stability of the species present in solution are also poorly defined, and until quite recently very little was known about them. The distribution of species is governed by two inter-

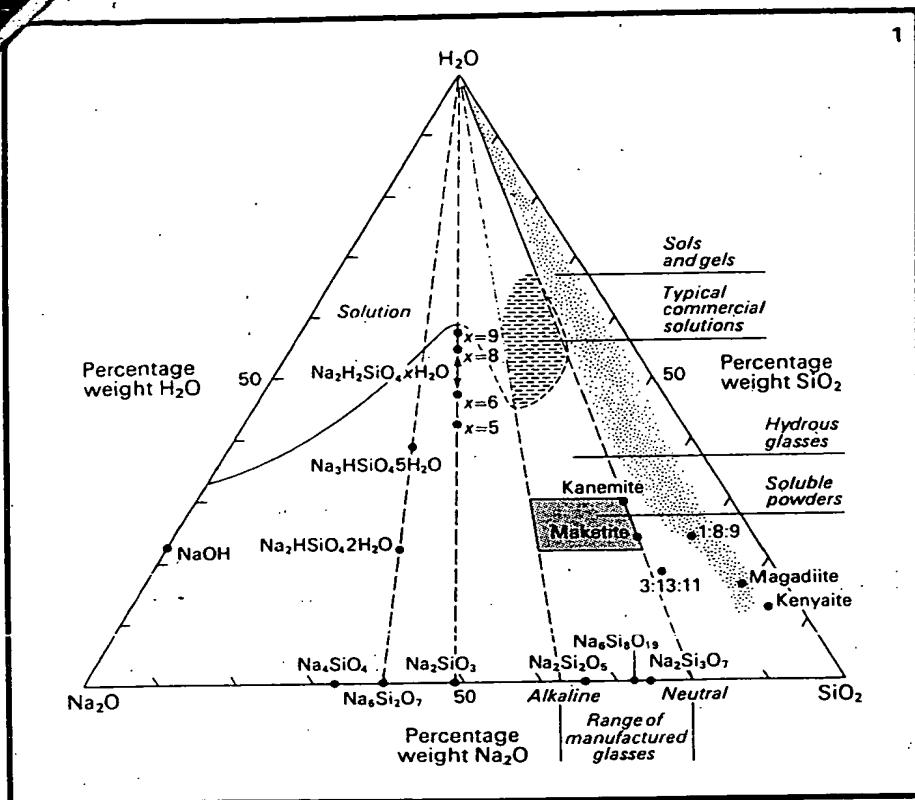
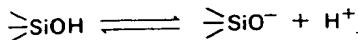
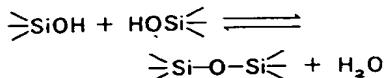


Fig. 1. Phases (including metastable ones) in the ternary system Na_2O - SiO_2 - H_2O ; adapted from Barby et al.



and polymerisation-depolymerisation:



Unlike the similar reactions in phosphate solutions, the latter proceeds very readily making silicate solutions very difficult to study; even the pK values for the various species are not precisely known. However the development and application of powerful ^{29}Si nmr techniques over the past few years⁴ has revolutionised our knowledge of the species present. Combining this information with that from other techniques such as laser Raman spectroscopy and trimethylsilylation has further clarified our ideas.

Figure 2, adapted from earlier work,¹ summarises the situation. Below pH 9, the solubility of all forms of silica is very low; that depicted in the figure is for the most soluble form, amorphous silica. (The solubility of quartz and other crystalline forms is considerably lower.) The species in solution in equilibrium with this is monomeric and, since silicic acid is very weak ($pK=9.4$), virtually totally protonated.

Above pH 9, dissociation becomes significant and the solubility correspondingly increases. With increasing concentration, polymerisation into multinuclear species also becomes important, and solutions above about 0.1 M with respect to silicon generally contain a complicated mixture of species in

dynamic equilibrium. In the area to the top right of Fig. 2, changes in pH or concentration result in very rapid adjustment of the species in solution and re-establishment of equilibrium. These species are thus quite labile. It has recently been shown⁴ that contrary to the expectations of many workers in the field, a considerable number of these species (Fig. 3) are based on a ring of three silicate tetrahedra, hereafter called a 'three-membered ring' (although the ring actually contains six atoms—three Si and three O). This discovery was surprising because in crystalline solids such a ring is rare as an isolated entity and (with two exceptions, $\text{Ni}(\text{en})_3\text{Si}_6\text{O}_{15} \cdot 26\text{H}_2\text{O}$ and the mineral zussmanite) unknown as part of a larger silicate unit.

Studies on silicate solutions by the method of trimethylsilylation⁶ had sug-

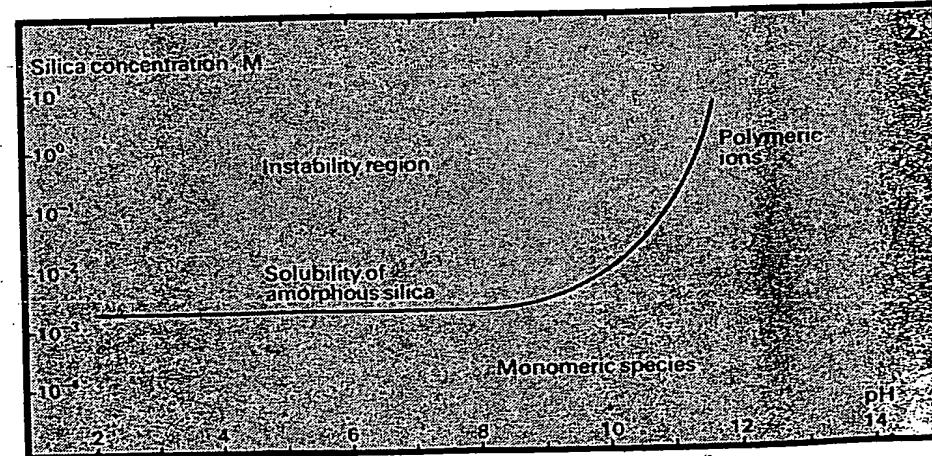
gested that the three-membered ring was unimportant in solution, and that the sequence of polymerisation was monomer \rightarrow dimer \rightarrow linear trimer (three-membered chain) \rightarrow cyclic tetramer (four-membered ring) \rightarrow cage-like units (Fig. 3c). It now seems that this result was an artefact of the method. The sequence is in fact probably correct for polymerisation occurring to the left of the solubility curve in Fig. 2, that is in the less alkaline region of unstable solutions, but to the right of the curve the three-membered ring appears stable, and species such as those depicted in Fig. 3(b) occur. These species are labile, and re-equilibrate rapidly with change of pH or concentration within the region of polymeric species; because of the reluctance of extended structures to incorporate three-membered rings, they are probably limited in size. Larger units such as are found in sol and gel particles are probably based on four-membered and larger rings, and are less labile.

Sols and gels

The area to the top left of Fig. 2 represents conditions under which all solutions are ultimately unstable with respect to precipitation of amorphous silica or silica gel and has been termed the instability region. The rate at which apparent equilibrium is attained is very variable: acidification of fairly concentrated—ca molar—sodium silicate solutions to a pH of about 5 or 6 produces a stiff gel virtually instantaneously; at pH values greater or less than this the time to form a gel increases by several orders of magnitude. It is possible to prepare apparently clear solutions that persist for weeks or months before becoming opaque and finally gelling.

Careful reduction of pH by lectrodialysis or ion exchange (keeping electrolyte concentration low) can produce slightly alkaline sols, with a soda-silica ratio of 1:30 or more, containing monodisperse negatively charged particles of ca 2–10 nm, the size being determined by the preparative technique used. These include the silica sols of commerce, and may be clear in appearance or more or less opalescent, depending on particle size. The stability

Fig. 2. Summary of silicates in solution, drawn from a variety of sources.



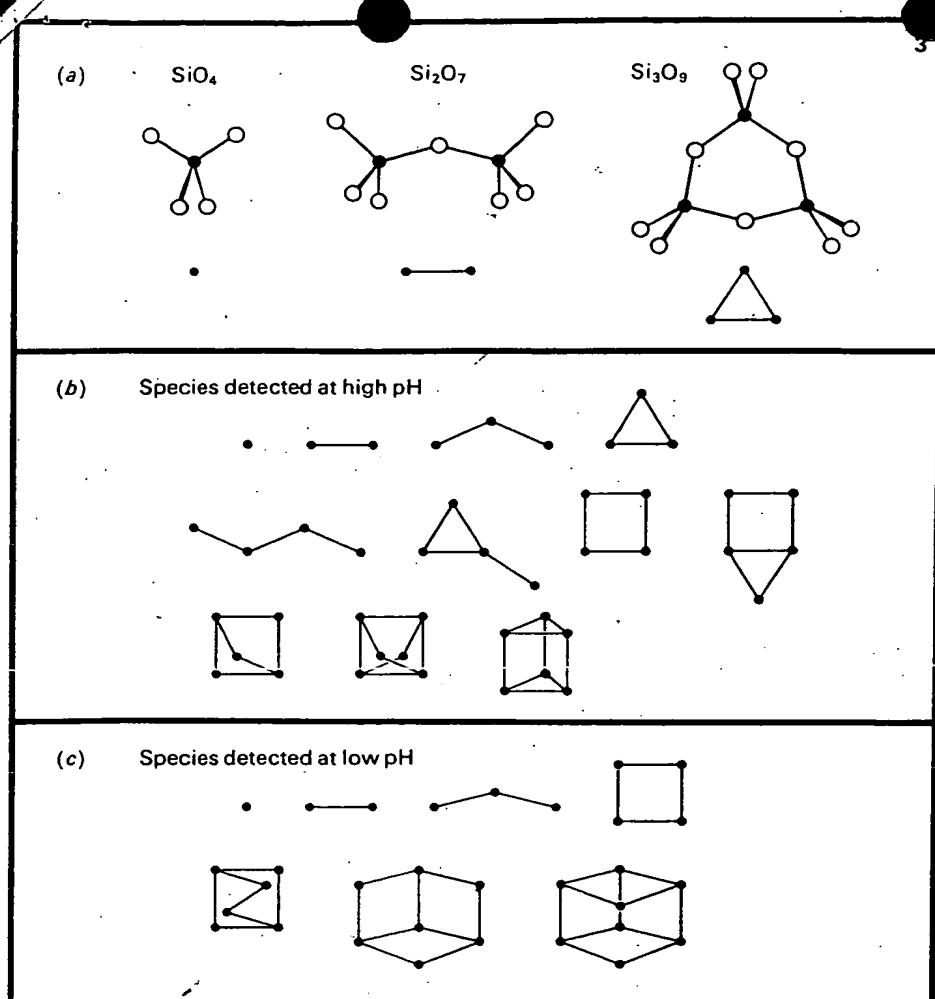


Fig. 3. Some silicate species found in solution: (a) Monomer, SiO_4 , dimer, Si_2O_7 , and cyclic trimer, Si_3O_9 (ionic charge etc omitted for simplicity; the state of protonations depends on pH). Diagrammatic representations showing the silicon atoms are given below the conventional drawings; the latter get very complicated for higher degrees of polymerisation. (b) Species found in alkaline solution, depicted using the convention shown in (a). (c) Species detected in acid solutions.

of these (in the sense of persistence rather than true thermodynamic stability) is greatly influenced by the presence or absence of electrolyte; addition of salt to a sol or a solution in the instability region results in the precipitation of silica.

The particles in silica sols are spherical, and electron microscopic examination of gels shows that these too are based on roughly spherical particles, generally about 100 Å in diameter which are themselves composed of still smaller particles, about 15 Å in diameter. Opal—naturally occurring silica gel—consists of regular arrays of very much larger particles, apparently also based on hierarchies of smaller spherical particles.⁶ The diameters of the larger particles are of the order of the wavelength of visible light, and the unique 'fire' of opal is an optical effect analogous to the diffraction of x-rays by crystals.

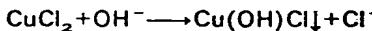
The detailed internal structure of the small spheres is not known, but it is tempting to suppose that they are extended versions of the cage-like structures shown in Fig. 3(c). It seems unlikely that they are based on strings or

ribbons of silica tetrahedra, as has sometimes been suggested.⁷ Such structures could certainly curl up to give spherical particles, but it seems probable that cross-linking would then follow, so that the end product would be linked in three dimensions anyway. Model building⁸ shows that structures based on four and five membered rings are compatible with many of the observed properties of the larger silicate species found in solution; the proportion of five-membered rings increases as the size of the particle increases. If the five-membered ring is indeed favoured in large silica or silicate particles, the reluctance of many of these structures to crystallise might be a consequence of the well-known incompatibility of five-fold symmetry with infinitely repeating structures. In contrast, it is perfectly compatible with the production of approximately spherical units (Fig. 4).

How does your garden grow?
We cannot leave the subject of precipitation from soluble silicates without referring to that most attractive experiment in which crystals of various soluble salts (group II and transition metal salts

are particularly suitable) dropped into a silicate solution produce a 'chemical garden' (Fig. 5). The often fantastic growths that appear resemble organic structures, and with a little care most artistic effects can be produced. It has long been realised that reaction between the salt and the solution precipitates an effectively semi-permeable membrane, through which water is drawn by osmosis as the salt within continues to dissolve. The internal pressure eventually ruptures the membrane, the salt solution thus released reacts with the external silicate solution producing more membrane, and so the growth continues. The rate of growth is roughly proportional to the solubility of the salt.

The chemical composition of the membranes is less well appreciated. They are frequently stated to be 'insoluble silicates', which is certainly not correct for most of the salts used. A recent publication⁹ considers that they are mixed hydrous oxides of uncertain composition. However, for copper salts they can be shown to be mixtures of the corresponding basic copper salt and silica gel.⁹ It appears that the dissolving salt reacts with the alkaline silicate solution, e.g.:



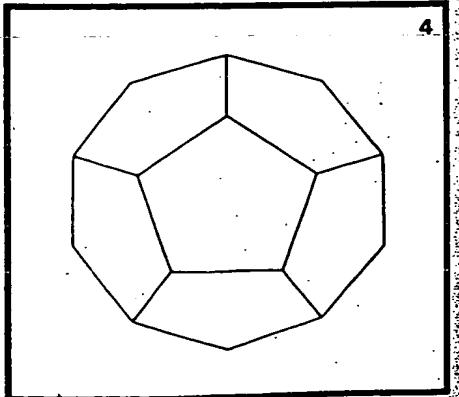
The consequent reduction in pH brings the silicate solution into the instability region causing silica gel to precipitate, intimately mixed with the basic copper salt. Similar mechanisms probably apply in other cases.¹⁰

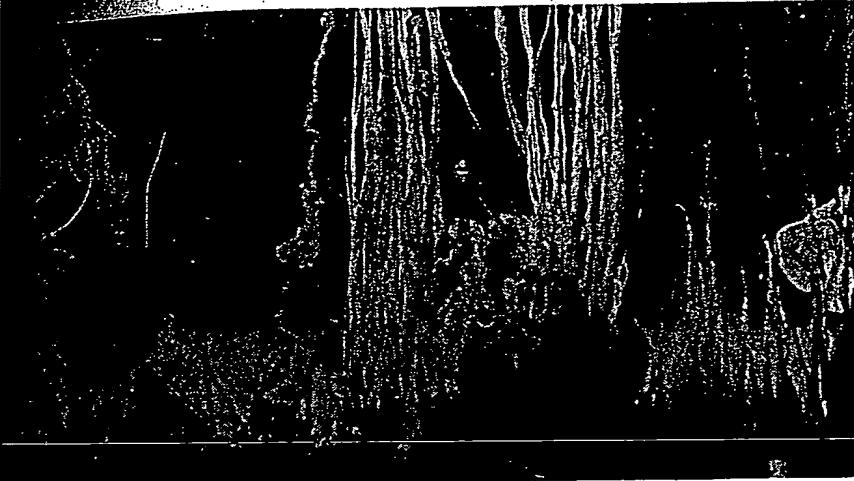
Future developments

What future developments can we expect to see in the field of soluble silicates? From the point of view of fundamental chemistry, the complete description of the species in solution through sets of pK values and equilibrium constants for the various polymeric species, for so long little more than a pipe dream, seems now to be not so very far away. It might be thought that understanding of the process of sol and gel formation would automatically follow, but recent evidence¹¹ shows that gelation and polymerisation are not directly

Fig. 4. A pentagonal dodecahedron, showing how five-fold symmetry is compatible with finite spherical units. A similar unit, built from silicate tetrahedra, has

external dimensions of about 16 Å.





A 'silicate garden': photograph courtesy Unilever Research.

ect d. Application of dynamic light scattering, ultrafiltration and electron microscopy all show promise for studying formation and structure of the final products.

On the technical side, we can expect effort to be put into reducing the energy used in production. For example, method of dissolving glass conveniently at ambient pressure has been devised;¹² more efficient furnace in and better utilisation of waste heat (eg. to preheat raw materials), are other possibilities.

The consumption of silicates for detergents will probably increase.

Since the release of phosphate in effluent water is strongly discouraged in many countries it may be partially replaced by silicate, even though the latter, unlike phosphate, is not an efficient sequestering agent for calcium. Zeolites can also be used to provide a 'built in' water softener for detergents. For this and other reasons production of zeolites, at present a very minor use of sodium silicate (Table 1), will almost certainly increase. The potential of zeolites in petroleum cracking has by no means been fully exploited.

As petroleum prices continue to rise, we can expect to see greater pressure to

substitute inorganic binders for organic ones. Tiles and composites based on soluble silicate adhesives, and the use of soluble silicate as a vehicle in specialist paints will become increasingly economic; such totally inorganic materials have the additional advantage of complete non-flammability. Not for nothing are man's oldest artefacts and many of his most enduring structures based on silica.

References

- D. Barby *et al* in *The modern inorganic chemicals industry*, R. Thomson (ed), p 320. London: Chemical Society, 1977.
- R. Schmid, G. Huttner and J. Felsche, *Acta Crystallogr.*, 1979 **B35**, 3024.
- H. Annealed and L. Fält, *Fifth int. conf. zeolites, recent progress reports and discussion*; R. Sersale, C. Coletta and R. Aiello (eds), p 5. Naples: Giannini, 1981.
- R. K. Harris, C. T. G. Knight and W. Hull, *J. Am. Chem. Soc.*, 1981, **103**, 1577.
- L. S. Dent Glasser and E. E. Lachowski, *J. Chem. Soc. Dalton Trans.*, 1980, 399.
- P. J. Darragh, A. J. Gaskin and J. V. Saunders, *Sci. Am.* 1976, **234**, 84.
- M. F. Bechtold, R. D. Vest and L. Plambeck, *J. Am. Chem. Soc.*, 1968, **90**, 4590. See also R. K. Iler, *The chemistry of silica*. New York: Wiley 1979, for a complete discussion of polymerisation theories.
- R. D. Coatman, N. L. Thomas and D. D. Double, *J. Mater. Sci.* 1980, **15**, 2017.
- L. S. Dent Glasser and S. P. Hepburn, unpublished work.
- T. H. Hazlehurst, *J. Chem. Educ.*, 1941, **18**, 286.
- L. S. Dent Glasser and D. N. Smith, *J. Chem. Soc. Chem. Commun.*, 1980, 727.
- F. R. Jorgensen, *J. Appl. Chem. Biotechnol.*, 1977, **27**, 303.

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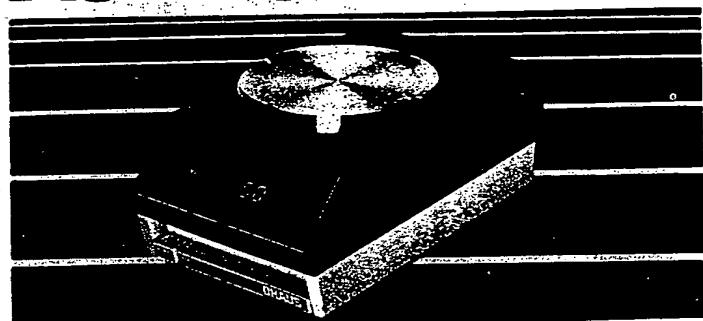
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ised, and colloidal silicate for that part not detected; it is to be understood that these terms cover a range of sizes, and that the ranges probably overlap.

If conversion of each silicate species in the solution into its corresponding derivative were quantitative, the technique would provide a precise method of studying the distribution of species in solution. Unfortunately, this is almost certainly not the case. The critical step is probably the acidification of the solution, which must be accomplished as rapidly as possible to avoid polymerisation of the silicate groups.^{11,12} The more concentrated the solution, the more difficult it is to do this, and solutions more concentrated than ca. 1 mol dm⁻³ with respect to silicon can be handled only with great difficulty. Comparison with ²⁹Si n.m.r. data¹⁴ suggests that orthosilicate in particular may be lost during the reaction, although the ratio of this to more condensed species is in fair agreement with that obtained from n.m.r. spectroscopy. Results from trimethylsilylation studies are therefore only semi-quantitative. Despite this limit, trimethylsilylation studies provide valuable information about silicate solutions that cannot be obtained by other chemical methods.

In the present work the technique was used to check previous reports on the rate of equilibration and to study the changes in the distribution of silicate species that occur when sodium silicate solutions are subjected to: (1) dilution; (2) change in pH by the addition of acid or alkali; and (3) removal of sodium ion by ion exchange. The dissolution of crystalline sodium metasilicate was also studied.

EXPERIMENTAL

Preparation of Sodium Silicate Solutions

Solutions were prepared in CO₂-deionised water from the following silicates: Na₄H₄SiO₄·H₂O prepared from sodium metasilicate pentahydrate (B.D.H.) by recrystallisation as described previously;¹¹ Na₄SiO₄ prepared by drying Na₄SiO₄·8H₂O at 200 °C and then heating at 600 °C for 2 h (solutions prepared from these two sources have mol ratio Na₂O : SiO₂ = 1 : 1); and Pyramid brand No. 1 sodium silicate solution (Joseph Crucible and Sons, Ltd), which has a Na₂O : SiO₄ mol ratio 1 : 3.41 and is ca. 0.8 mol dm⁻³ in silicon.

The solutions were stored in tightly stoppered glass bottles that were opened only briefly for sampling in order to avoid contamination by atmospheric CO₂. Solution concentrations are given in terms of their molarity in silica. They were analysed for sodium and silicon using a Varian-Eliel model 305 atomic absorption spectrophotometer.

Preparation and Estimation of Trimethylsilyl Derivatives.

The trimethylsilylation procedure used was that described by Lantz,¹⁵ in which the reagent is a mixture of hexamethyldisiloxane, tripropyl aluminium, and hydrochloric acid. The silicate solutions were added dropwise to the vortext of a rapidly stirred reagent mixture. Turbulent mixing, using either buffered vessels or an ultrasonic mixer, did not give significantly different results. Low-atomic-weight species were studied by g.c., as described previously;^{11,12} where these species only were to be studied, quantities used

were only one tenth of those given by Lentz. The principal species, and that the ranges probably overlap, were the derivatives of: orthosilicate groups, or monomer, as in equation (1) (designated Si₁); polysilicate groups, or dimer, as in (2) (Si₂); linear trimer (Si₃); cyclic tetramer (Si₄); several hexameric species not readily separable by g.c.;¹⁶ (Si₅) and an octamer, Si₈O₁₆, with a cage-like structure in (Si₆). Only insignificant amounts of derivatives of the cyclic trimer postulated from n.m.r. spectroscopy¹⁴ were found. However, it is possible that in solution the ring form exists in equilibrium with the linear form of the trimer, and that the latter trimethylsilylates more readily and is thus the only form detected. The trimethylsilylated ring derivative is quite difficult to prepare even from crystalline solids known to contain Si₆ rings; this might indicate that the derivative is sterically hindered, although it might also mean that the ring, which is thought to be strained,¹⁷ only opens to a chain when released from the confines of a crystal structure.

Where the higher-molecular-weight polysilicate fraction was to be studied by g.c., larger scale preparations were needed, and for economy only a few of these were made. After reaction, a portion of extract was retained for study by h.p.c., and the solvent distilled from the remainder. The residue was dried at 115 °C. All or some of the monomer and dimer derivatives were lost in the process (the amount could be estimated by g.c.), the loss decreasing as the molecular weight and degree of cross-linking of the polysilicate increases (presumably through physical trapping of the small species by the larger). The polysilicate fraction thus consists mainly of species from the trimers upwards.

In timed experiments, the reagents for trimethylsilylation were prepared in advance, and the sample withdrawn and immediately added to the stirring mixture.

Flow-time Measurements.—These were used to compare viscosities, as a check on the results from other methods.

A Hewlett-Packard 501B Auto Viscosimeter with a GUDA Programmer was used. All solutions, water, flasks, and viscometers were stored in the thermostatted bath used for silicate pentahydrate (B.D.H.) by recrystallisation as described previously;¹¹ Na₄SiO₄ prepared by drying Na₄SiO₄·8H₂O at 200 °C and then heating at 600 °C for 2 h (solutions prepared from these two sources have mol ratio Na₂O : SiO₂ = 1 : 1); and Pyramid brand No. 1 sodium silicate solution (Joseph Crucible and Sons, Ltd), which has a Na₂O : SiO₄ mol ratio 1 : 3.41 and is ca. 0.8 mol dm⁻³ in silicon.

The solutions were subjected are shown in Figure 1, which is adapted from Stumm et al.,¹⁸ as modified by Hartley et al.¹⁹

The treatments are described below, and figures in square brackets relate to positions on Figure 1.

Dilution. A 0.8 mol dm⁻³ sodium silicate solution of 3.41 : 1 mol ratio [1] was quickly weighed into a standard flask. About 90% of the required water was added and titration started. The flask was stirred vigorously to disperse the viscous silicate solution as quickly as possible, made up to the mark and shaken again. For trimethylsilylation a sample was taken as soon as dilution was completed, further samples being taken at intervals. Solutions diluted to 0.12 and 0.1 mol dm⁻³ [3] were studied in this way.

Dissolution of Na₄SiO₄. Anhydrous sodium metasilicate was dissolved in a manner similar to the above to give a 0.125 mol dm⁻³ solution [4]. Because dissolution took some time, samples withdrawn for trimethylsilylation were also analysed for sodium and silicon.

Change in pH. The soda to silica ratio of a 0.1 mol

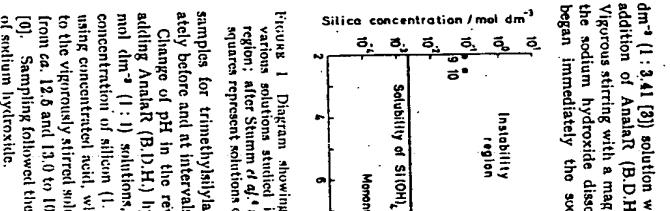


FIGURE 1 Diagram showing pH and concentration of the trimethylsilylation reaction, after Stumm et al.¹⁸ and Hartley et al.¹⁹ The numbered squares represent solutions discussed in the text

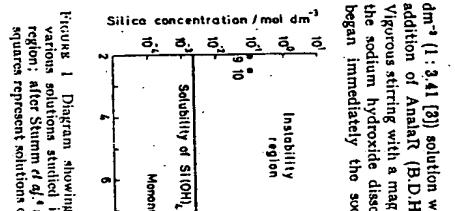


FIGURE 2 Distribution of low-molecular-weight species in a 1 : 3.41 solution after dilution

dm⁻³ (1 : 3.41 [3]) solution was changed to 1 : 1 [4] by the addition of AnalaR (B.D.H.) sodium hydroxide pellets. Vigorous stirring with a magnetic stirring bar ensured that the sodium hydroxide dissolved within 2 min. Timing began immediately the sodium hydroxide was added; obtained by correcting the polysilicate fraction, obtained by

addition to the volatile species (Si₁–Si₈) the total polysilicate as determined by weight is given. Table 1(b) gives the results of studies on the polysilicate species in solution, and also the values of \bar{N}_n and \bar{M}_w for all species obtained by

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homogeneity of the solution, and for dropwise addition to the reagents in the case of trimethylsilylation and filtration in the case of flow-time measurements, neither technique could be used to examine the solution less than 5 min after dilution.

These results seem to show that changes in the solution happen rapidly, both to small and large species. On the other hand, we have noticed differences in the distribution of low-molecular-weight species found in solutions of apparently identical composition made by diluting

TABLE 3

| Distribution of low-molecular-weight species in a 1 : 3.41 solution after dilution from 6.8 to 0.1 mol dm ⁻³ SiO ₄ | | | | | | |
|------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Time min | Percentage SiO ₄ recovered as: | | | | | |
| | Si ₁ | Si ₂ | Si ₃ | Si ₄ | Si ₅ | Si ₆ |
| 0 | 35 | 7 | 3 | 3 | 6 | 3 |
| 5 | 55 | 25 | 11 | 6 | 4 | 0 |
| 10 | 60 | 24 | 10 | 6 | 4 | 0 |
| 15 | 60 | 22 | 11 | 8 | 4 | 0 |
| 20 | 60 | 22 | 10 | 7 | 4 | 0 |
| 30 | 32 | 7 | 4 | 3 | 6 | 3 |
| 40 | 30 | 8 | 3 | 2 | 6 | 3 |
| 50 | 33 | 7 | 4 | 3 | 6 | 3 |
| 60 | 30 | 8 | 3 | 2 | 6 | 3 |
| 120 | 33 | 7 | 4 | 3 | 6 | 3 |
| 300 | 30 | 8 | 4 | 3 | 6 | 3 |
| 1440 | 35 | 7 | 4 | 3 | 6 | 3 |
| 2880 | 30 | 7 | 4 | 3 | 6 | 3 |

different batches of commercial silicate solution;¹¹ indeed, the solution used in the present studies yields a significantly higher proportion of monomer than that used previously.¹¹ The two observations are not in fact irreconcilable. All the solutions lie close to the boundary of the instability region, and probably contain significant amounts of colloidal material. The size of such particles could depend on the exact conditions under which the glass had been dissolved in the course of their production, or perhaps on the amount of iron (always present in commercial solutions) or the extent of CO₂ contamination.

If very large particles such as these participate in solution equilibria only through their surfaces, the time taken for equilibrium to be established will be determined by the rate of diffusion of acid across the particle surface. If the particles are spherical, the time taken for equilibrium to be established will be proportional to the square of the radius of the particle. Thus, if the radius of the particles is increased by a factor of 2, the time required for equilibrium to be established will increase by a factor of 4. The time taken for equilibrium to be established will also depend on the concentration of acid, and on the concentration of silicate ions in the solution.

TABLE 4

| Distribution of low-molecular-weight species on dissolving anhydrous Na ₂ SiO ₄ | | | | | | |
|-------------------------------------------------------------------------------------------------------|-------------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Time min | Percentage SiO ₄ recovered as: | | | | | |
| | Total Si ₁ | Si ₂ | Si ₃ | Si ₄ | Si ₅ | Si ₆ |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 42 | 11 | 7 | 10 | 0 | 0 |
| 10 | 46 | 22 | 10 | 8 | 0 | 0 |
| 20 | 42 | 20 | 0 | 8 | 0 | 0 |
| 40 | 42 | 22 | 13 | 7 | 1 | 0 |
| 80 | 40 | 22 | 13 | 7 | 1 | 0 |

(Additional determinations made after 30, 120, and 480 min did not differ significantly.)

effective contribution of (say) two 500-unit particles would be greater than that of one J 100-unit particle by a factor of $2 \times 500/1 = 1000$, assuming that the particles are roughly spherical with radii proportional to the cube root of the number of silicate units they contain. Such a situation represents only quasi-equilibrium, but it is apparent that true equilibrium would be approached extremely slowly, in accord with earlier conclusions about the instability region.

Dissolution Experiment.—Table 4 gives the distribution of low-molecular-weight species at intervals after

the addition of anhydrous sodium metasilicate to water. The constitution of the solution became essentially constant within 5 min, although complete dissolution took over 10 min. The break-up of the infinite chains in the Na₂SiO₄ crystals seems to be instantaneous.

Change of pH.—Table 5 gives the results of adding

NaOH to a 1 : 3.41 solution, predicted by addition of

TABLE 5

| Time min | Percentage SiO ₄ recovered as: | | | | | |
|-------------|-------------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | Total Si ₁ | Si ₂ | Si ₃ | Si ₄ | Si ₅ | Si ₆ |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 55 | 25 | 11 | 6 | 4 | 0 |
| 10 | 60 | 24 | 10 | 6 | 4 | 0 |
| 15 | 60 | 22 | 11 | 8 | 4 | 0 |
| 20 | 60 | 22 | 10 | 7 | 4 | 0 |
| 30 | 32 | 7 | 4 | 3 | 6 | 3 |
| 40 | 30 | 8 | 3 | 2 | 6 | 3 |
| 50 | 33 | 7 | 4 | 3 | 6 | 3 |
| 60 | 30 | 8 | 3 | 2 | 6 | 3 |
| 120 | 33 | 7 | 4 | 3 | 6 | 3 |
| 300 | 30 | 8 | 4 | 3 | 6 | 3 |
| 1440 | 35 | 7 | 4 | 3 | 6 | 3 |
| 2880 | 30 | 7 | 4 | 3 | 6 | 3 |

Figure 1). Table 6(a) and 6(b) gives the result of a pH change in the opposite direction, adding hydrochloric acid to 0.1 and 0.5 mol dm⁻³ (1 : 1) solutions (1440 and 550 to 750 and 600 respectively) on figure 1. In no case is any significant change observed after the first five

TABLE 6

| Time min | Percentage SiO ₄ recovered as: | | | | | | | |
|-------------|----------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|--------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | (a) 0.1 mol dm ⁻³ SiO ₄ ; pH changed from 12.50 to 10.70 on addition of acid | (b) 0.5 mol dm ⁻³ SiO ₄ ; pH changed from 13.00 to 11.00 on addition of acid | Total Si ₁ | Si ₂ | Si ₃ | Si ₄ | Si ₅ | Si ₆ |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 55 | 25 | 10 | 9 | 16 | 0 | 0 | R4 |
| 10 | 60 | 24 | 10 | 8 | 0 | 0 | 0 | 0 |
| 20 | 42 | 20 | 0 | 8 | 0 | 0 | 0 | 0 |
| 40 | 42 | 22 | 10 | 8 | 0 | 0 | 0 | 0 |
| 80 | 40 | 22 | 13 | 7 | 1 | 0 | 0 | 0 |
| 120 | 40 | 22 | 13 | 7 | 1 | 0 | 0 | 0 |
| 1440 | 40 | 22 | 13 | 7 | 1 | 0 | 0 | 0 |
| 2880 | 40 | 22 | 13 | 7 | 1 | 0 | 0 | 0 |

(Interim determinations at 30, 120, 300, and 1440 min did not differ significantly. * Samples taken immediately before addition of acid).

FIGURE 2

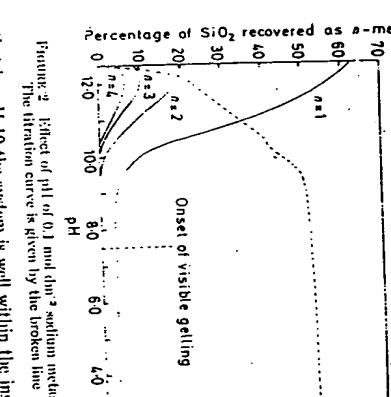


TABLE 7

Species recovered from silicate acid preparation

(a) Yields

(b) Average degree of polymerisation

(c) H

Corrected

 \bar{R}_n / \bar{R}_w

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Q

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After ageing for 72 h at room temperature, the sample contained only monomer, a trace of dimer, and polysilicate. Some gel or colloidal material was also present, and since this is not extracted the total yield was reduced. About twice as much polysilicate was recovered as from the freshly prepared sample, and its molecular weight and \bar{Q} value had both increased.

The results from the B series, in which 0.5 mol dm⁻³ (1 : 1) solution is simultaneously diluted and subjected to ion exchange, are harder to interpret. Comparison of the distribution of the volatile species from the original solution (B0) and the freshly prepared sample, and its molecular weight suggest that the structure of the solution is preserved, but this is not borne out by the polysilicate results [Table 7(b)], which show a considerable change in the degree of polymerisation. With ageing, the amount of polysilicate increases slightly and then decreases, but its structure as shown by M_n and \bar{Q} remains little changed. The total recovery drops, suggesting that colloidal silica is forming at the expense of the polysilicate. The amounts of volatile species also diminish steadily with ageing. Polysilicate thus behaves rather like the smaller intermediate species S_6 and S_7 in the titration experiment.

Differences in behaviour of the A and B series are most probably caused by the rather different distribution of species in the initial solutions. The results confirm that changes in solution at low pH are indeed comparatively small. Conclusions.—Despite the admitted limitations of the method of trimethylsilylation, it can be used to obtain significant information about the distribution of species in solution, and about changes in this. While recognising that the reaction itself may produce changes in the solution under test, rendering the results semi-quantitative rather than quantitative, we feel that the trends observed provide real information. For example it is difficult to believe that the maxima for certain species shown in figures 2 and 3, or the trends observable in Table 7, can be due solely to an artefact introduced by the technique.

Bearing this in mind we can draw the following conclusions.

(1) In alkaline solutions above pH ca. 10, the attainment of equilibrium is rapid, unless the solutions contain particles of colloidal dimensions. Even in solutions that do contain such particles, the smaller species rearrange rapidly to produce quasi-equilibrium. These results are in accord with those of earlier workers.

(2) Solutions produced by dissolving anhydrous Na_2SiO_3 (which contains SiO_4 chains) are, within the shortest time that can be measured, identical with those produced by dissolving $Na_4H_4SiO_4 \cdot 8H_2O$ (which contains solution (B0) and the freshly prepared sample, and its molecular weight suggest that the structure of the solution is preserved, but this is not borne out by the polysilicate results [Table 7(b)], which show a considerable change in the degree of polymerisation. With ageing, the amount of polysilicate increases slightly and then decreases, but its structure as shown by M_n and \bar{Q} remains little changed. The total recovery drops, suggesting that colloidal silica is forming at the expense of the polysilicate. The amounts of volatile species also diminish steadily with ageing. Polysilicate thus behaves rather like the smaller intermediate species S_6 and S_7 in the titration experiment.

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(3) In acid solutions at pH ca. 2 equilibrium is attained only very slowly. Again this is in accord with earlier work.

(4) As conditions in a solution are changed in the direction of increasing polymerisation, the amounts of a given polymerised species at first increase and subsequently decrease as successively more highly polymerised species form at its expense. Similar changes probably occur with time during the polymerisation of silicic acid at low pH.

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REFERENCES

- i F. Kübler, *Z. phys. Chem.*, 1909, 12, 171.
- ii J. G. Van, *Sodium Silicates*, Reinhold, New York, 1962.
- iii G. Lagerstrom, *Itra Chem. Stand.*, 1959, 13, 722.
- iv W. Stumm, H. J. Ijzer, and R. L. Chantlin, *Environ. Sci. Technol.*, 1967, 1, 221.
- v A. J. Walker and N. Whitelam, *J. Appl. Chem.*, 1969, 16, 230.
- vi H. C. Hünig, *Angew. Chem. Int. Ed. Engl.*, 1974, 13, 495.
- vii G. Engelsdorf, D. Ziegler, H. Jancke, D. Hoefel, and W. Wicker, *Z. anorg. Chem.*, 1976, 418, 17.
- viii R. K. Harris and R. H. Newman, *J.C.S. Faraday Pt. 1*, 1977, 103, 204.
- ix C. W. Lentz, *Inorg. Chem.*, 1964, 3, 514.
- x L. S. Dent Glasser and S. K. Shurina, *Br. Polym. J.*, 1974, 6, 245.
- xi L. S. Dent Glasser, E. V. Lachowski, and G. C. Cameron, *J. Appl. Chem. Biotechnol.*, 1977, 27, 30.
- xii K. K. Her and P. S. Philpot, *Ind. Eng. Chem.*, 1947, 39, 1570.
- xiii R. K. Harris and J. Jones, personal communication.
- xiv S. K. Shurina, L. S. Dent Glasser, and C. T. Mason, *J.C.S. Dalton*, 1978, 134.
- xv D. H. Hinchliffe, G. Gunter, G. Engelsdorf, H. Jancke, P. Fränkle, and W. Wicker, *Z. anorg. Chem.*, 1976, 424, 115.
- xvi L. S. Dent Glasser, R. K. Harris, J. Jones, and E. E. Lachowski, *J. Mat. Structure*, 1978, 51, 219.
- xvii M. O'Keefe and B. G. Hyde, *Acta Cryst.*, 1978, B34, 27.
- xviii D. Hinchliffe, T. Griffiths, A. R. Jacques, and D. Dawson, *Soluble Silicates and Their Derivatives*, in *The Modern Inorganic Chemicals Industry*, ed. R. Thompson, The Chemical Society, London, 1971.
- xix G. H. Alexander, *J. Amer. Chem. Soc.*, 1953, 75, 2917.
- xx L. S. Dent Glasser, J. A. Gard, and E. E. Lachowski, *J. Appl. Polym. Sci.*, 1963, 7, 209.
- xxi G. H. Alexander, *J. Amer. Chem. Soc.*, 1954, 76, 2004.
- xxii R. K. Her, *J. Phys. Chem.*, 1963, 67, 604.

Silicate Species in Solution. Part 2.1 The Structure of Polymeric Species

By Lesley S. Dent Glasser* and Eric E. Lachowski, Department of Chemistry, University of Aberdeen, Merton Walk, Old Aberdeen AB9 2UE

The following rules are formulated concerning the structure of polymeric species in solution: (1) connectivity is maximised consistent with a lower ring size of four tetrahedra (except possibly in trimeric species); (2) all tetrahedra in a given species show as nearly as possible the same degree of connectivity. Both these rules are consistent with the idea that the ability of silicate groups in solution decreases with increasing connectivity.

Attempts to formulate all possible silicate species, either by abstract pencil-and-paper chemistry or through building models, produce a bewildering variety of structures and at first sight the task of rationalising these seems hopeless. However, the experimental results indicate that surprisingly few species actually occur in solution, and the problem then looks more tractable.

Figure 1, which is explained in detail below, illustrates this. Each point marks a possible composition for a finite silicate species. Those that are believed to occur in sodium silicate solutions are distinguished as squares with formulae written beside them; other observed species, mainly those found in crystals, are marked as solid circles. The total number of observed finite species is quite small, and the number of finite species identified in solution is very small indeed.

REPRESENTATION OF SILICATE SPECIES

Each point on figure 1 represents a possible, in principle hypothetical, low-molecular-weight (*i.e.* finite) silicic acid $mH_2O \cdot nSiO_4$, where m and n are integers. The acid form is used merely for convenience; the species actually present in alkaline solution are the corresponding more-or-less deprotonated ions, and those found in solids are usually totally deprotonated. From here on the term 'species' will be used to mean a given silicic acid or any ion derived from it; that is, to refer to the Si-O skeleton only.

It is assumed that the normal rules of silicate chemistry are obeyed; each silicon is co-ordinated tetrahedrally by four oxygen atoms and these tetrahedra may share corners but not edges. Thus the lowest-molecular-weight species is that with $m = 2$ and $n = 1$, *i.e.* H_2SiO_4 , orthosilicic acid or 'monomer' (S_1 , in Part 1). The next member is that with $m = 3$, $n = 2$, *i.e.* $H_3Si_2O_7$, pyrosilicic acid or 'dimer' (S_2 , in Part 1).

Beyond this we reach either $m = 4$, $n = 3$, *i.e.* $H_4Si_3O_10$, linear trimer (S_3 , in Part 1), or $m = 3$, $n = 3$, *i.e.* $H_3Si_3O_9$, cyclic trimer or three-membered ring.[†] Note that these are molecular, not empirical, formulae; they all represent possible finite species. Infinite chains,

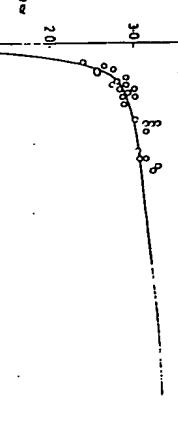
* Present address: University of Alberta, Edmonton, Alberta, Canada T6G 2E9.

[†] Three-membered ring, and similar terms here mean rings containing three tetrahedral units, not rings of three atoms.

where there exist as finite entities, we shall refer to them as 'cyclic trimer' and so on, but these terms are not appropriate for rings that form part of a more extended structure.

bias, the task was given to two volunteers with no knowledge of silicate chemistry. They were provided with plenty of tetrahedra and flexible bonds for connecting them, told the rules to be followed and asked to construct as large a variety of structures consistent with them as they could. For each model produced, \bar{Q} and n were determined.

The results are shown in Figure 3, together with the



values of n , obtained from models built according to the rules given in the text, compared with the experimental curve

of high-molecular-weight species invariably gave an H:C ratio greater than the 3:1 required by methyl groups (Part 1), and this too suggests the presence of unreacted silanol groups within the structure.

Finally we note that the shapes of the larger units are

consistent with the appearance noted for the primary particles of silica gel,¹⁰ while the structures postulated for the smaller species bear a striking resemblance to many of the 'secondary' building units that have been described for zeolites.¹⁰

Our thanks are due to Jill and Vicki Glasser for acting as a computer surrogate. Their enthusiastic production of models to test the theory is gratefully acknowledged.

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REFERENCES

- Part 1, L. S. Dent Glasser and E. E. Lachowski, preceding paper.
- R. K. Harris and R. H. Newman, *J.C.S. Faraday II*, 1977, 73.
- M. O'Keefe and B. C. Hyde, *Acta Cryst.*, 1978, **B34**, 27.
- C. G. Glidewell, *Inorg. Chim. Acta*, 1977, **25**, 77.
- F. Jelani, *Angew. Chem., Int. Ed.*, 1976, **15**, 418.
- L. S. Dent Glasser, L. Kifayat, H. Janke, P. Francke, D. Hoehnel, G. Garren, E. Engelman, H. Janke, P. Francke, and W. Wicker, *Z. anorg. Chem.*, 1970, **424**, 115.
- G. D. Parfitt and K. S. W. Sing, Academic Press, London, 1970.
- W. M. Alster, 'Molecular Sieves,' Society of Chemical Industry, London, 1968, p. 10.

RESULTS AND DISCUSSION

After stirring a mixture of $Hg(CCl_4)Ph$ and $[Co(CO)_4]$ at 60 °C or 2 h the major product was found to be $[Co_3(CO)(CCl_4)]$ (49%), together with $CoCl_4$, $HgCl_4$, and some $Co_2(CO)_6$ (15%), which is always formed to some extent on heating $[Co_3(CO)_6]$. Unlike the reaction in polar solvents no $Hg[Co(CO)_4]_2$ was detected among the products. When this reaction was repeated under similar conditions but in the presence of an excess of the carbene trap cyclohexene the yield of $[Co_3(CO)(CCl_4)]$ was reduced to 16%, and 7,7-dichloronorbornane was detected among the products by g.l.c. analysis. Other products of the reaction included $CoCl_4$, $HgCl_4$, $HgPbCl$ (7%), and $HgPb_2Cl$ (8%). The formation of the norcarane and the reduced yield of the cluster complex is evidence that at 60 °C not only is dichlorocarbene being generated by thermal decomposition of $Hg(CCl_4)Ph$, but that the carbene may be involved in cluster formation.

of the resulting species, although it should be remembered that details may differ with pH. Larger species are definitely not chain-like; on the contrary, they tend to form cage-like structures, probably rather globular, and as highly condensed as possible. Surface Q^1 groups, and to a lesser extent Q^2 groups, provide reactive growth points. Larger species thus tend to contain mainly Q^2 and Q^3 units, with a \bar{Q} value of ca. 3.5 for very large values of n . Since the limiting value of \bar{Q} is not 4, even when n tends to ∞ , some unattached corners must remain as silanol groups trapped within the structure and unable to condense. Analyses of trimethylsilyl derivatives of high-molecular-weight species invariably give an H:C ratio greater than the 3:1 required by methyl groups (Part 1) and this too suggests the presence of unreacted silanol groups within the structure.

Finally we note that the shapes of the larger units are consistent with the appearance noted for the primary particles of silica gel,¹⁰ while the structures postulated for the smaller species bear a striking resemblance to many of the 'secondary' building units that have been described for zeolites.¹⁰

Metal Carbonyl Chemistry. Part 27.¹ Formation of $[Co_3(CO)(CO)]$ by Reaction of the Carbene Precursor $Hg(CCl_4)Ph$ with Octacarbonyldicobalt

By Brian L. Booth,* Geoffrey C. Casey, and Robert N. Haszeldine, Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1GD

Ostacarbonyldicobalt reacts with the dichlorocarbene precursor $Hg(CCl_4)Ph$ at 60 °C in hexane to afford $[Co_3(CO)(CO)]$ in 95% yield. A similar yield of this complex is also obtained at 30 °C, i.e. under conditions where appreciable thermal decomposition of $Hg(CCl_4)Ph$ to $HgPbCl$ and CCl_4 does not occur. Trapping experiments using cyclohexanes have demonstrated that under both sets of conditions dichlorocarbene is formed. Possible mechanisms to explain the formation of the carbene and $[Co_3(CO)(CO)]$ are discussed.

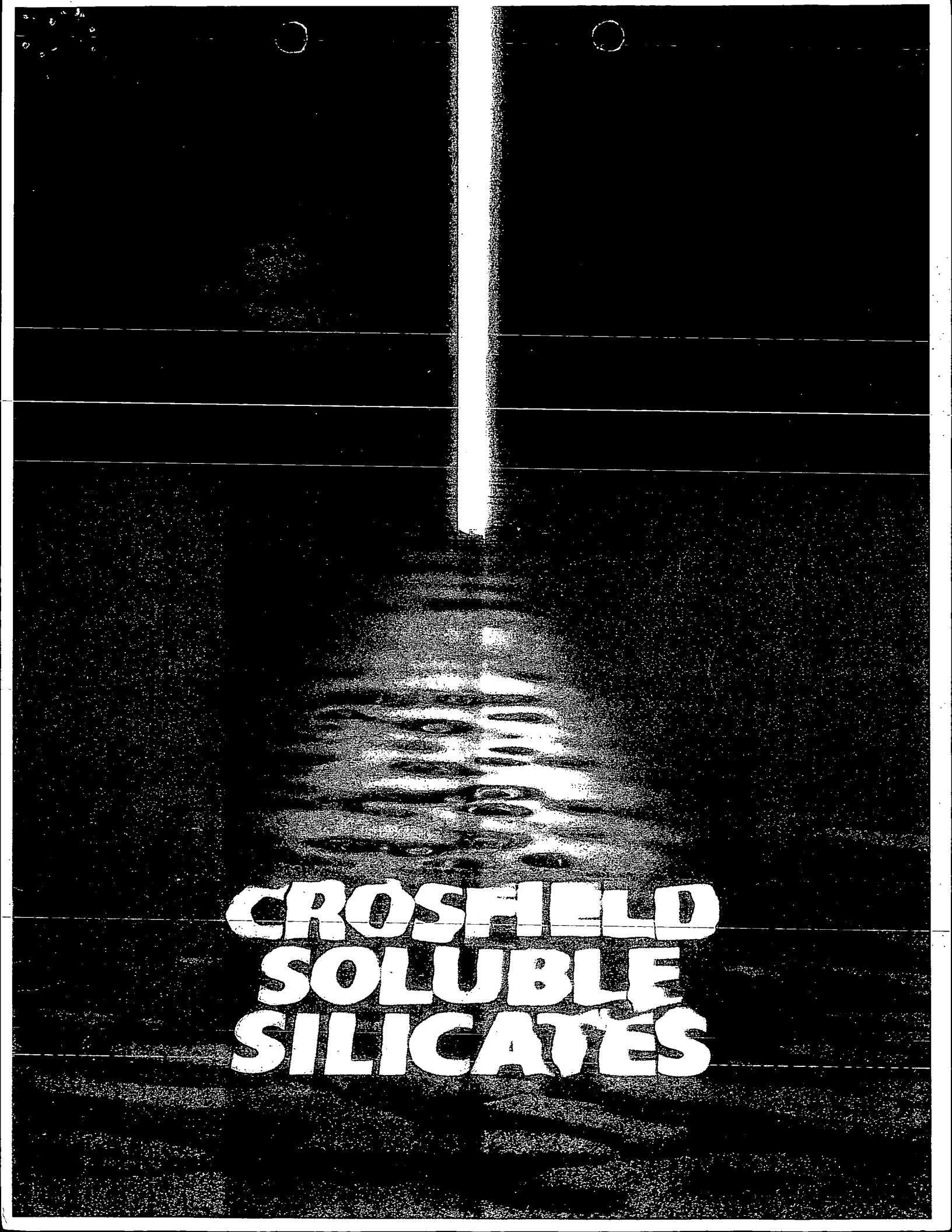
Dichlorocarbene has been detected recently as one of the intermediates formed when octacarbonyldicobalt and the polyhalogenomethanes CCl_4 , $CBiCl_4$, or CBi_2Cl_4 react in the non-polar solvent hexane to give the non-acetylenic methyltriobicarbonyl cluster complex $[Co_3(CO)(CO)]$ as the major product.² In an effort to clarify the mechanistic role of the carbene in the formation of the cluster complex, we have investigated the reactions of $[Co_3(CO)_6]$ with the carbene precursor $Hg(CCl_4)Ph$.

The only previous report of a reaction between these two compounds describes reactions carried out in the presence of carbon monoxide, which have not been investigated in any detail, but it is suggested that the appreciable concentration of $[Co_3(CO)_6]$ present under these conditions may lead to nucleophilic displacement of $-CCl_3$ from $Hg(CCl_4)Ph$, thus giving rise to $Hg[Co(CO)_4]_2$. This reaction has been shown to yield $Hg[Co(CO)_4]_2$, Ph_3CO , $CHCl_3$, and only a very small amount of $[Co_3(CO)(CO)]$. This reaction has together with carbon monoxide.³ This reaction has not been investigated in any detail, but it is suggested that the low yield of $[Co_3(CO)(CO)]$ observed⁴ in the present work the reactions were all carried out in hexane, i.e. under conditions where disproportionation to hexane is impossible, and a different mechanistic pathway might be anticipated.

As a further check the reaction between $Hg(CCl_4)Ph$ and $[Co_3(CO)_6]$ was repeated at the lower temperature of 30 °C. A control experiment using $Hg(CCl_4)Ph$ in the presence of cyclohexane showed that at this temperature there was no observable dissociation to give dichlorocarbene, and it was confidently anticipated that the reaction with $[Co_3(CO)_6]$ would not lead to cluster formation at this lower temperature. Surprisingly, not only was $[Co_3(CO)(CO)]$ formed, but the yield (61%) was comparable to that obtained at the higher temperature.

A careful examination of the reaction products showed the presence of the dichlorocarbene adduct $[Co_3(CO)(CO)](CCl_3)$ (44%) was not markedly affected, although the yield of $Hg(CCl_4)Ph$ (8%) together with a trace of the dichlorocarbene product, tetrachloroethylene. Furthermore, when this reaction was repeated at 30 °C but in the presence of cyclohexane the yield of $[Co_3(CO)(CO)]$ was only 44%.

In separate experiments it has also been demonstrated that the mixture of $Hg(CCl_4)Ph$ and $[Co_3(CO)_6]$ in hexane at both 60 and 30 °C is capable of initiating the polymerisation of a 1:1 molar mixture of styrene and methyl methacrylate; under similar conditions neither $Hg(CCl_4)Ph$ nor $[Co_3(CO)_6]$ alone cause polymerisation to occur. The yield of $[Co_3(CO)(CO)]$ (43%) at 60 °C, 36% at 30 °C, is only slightly affected, if at all, by the presence of the monomers, bearing in mind the experimental difficulties of isolating the cluster from the polymerised product mixture. The characterisation of the polymer from the reaction at 60 and at 30 °C as a 1:1 copolymer confirms a free-radical initiation step.⁵ Further evidence of this is provided by the fact that when these reactions were repeated under similar conditions, but in the presence of a three-fold excess of the radical scavenger 1,1-diphenyl-2-picrylhydrazyl, polymerisation was inhibited. From these results it is apparent that the interaction of $Hg(CCl_4)Ph$ with $[Co_3(CO)_6]$ both at 60 and 30 °C gives rise to an intermediate or intermediates which readily undergo homolysis to form CCl_4 , Cl , Ph , or $[Co(CO)]$ radicals. It is striking that in every respect these reactions very closely resemble the reactions of $[Co_3(CO)_6]$ with polyhalogenomethanes investigated previously,² suggesting that similar intermediates may be involved in both cases.



A black and white photograph showing a perspective view of a path or stream bed curving away from the viewer. The path is light-colored and appears to be made of sand or gravel. It leads towards a bright, overexposed area at the top of the frame, possibly a body of water or a clearing in the clouds. The surrounding terrain is dark and textured, suggesting rocks or dense vegetation. The overall composition is minimalist and atmospheric.

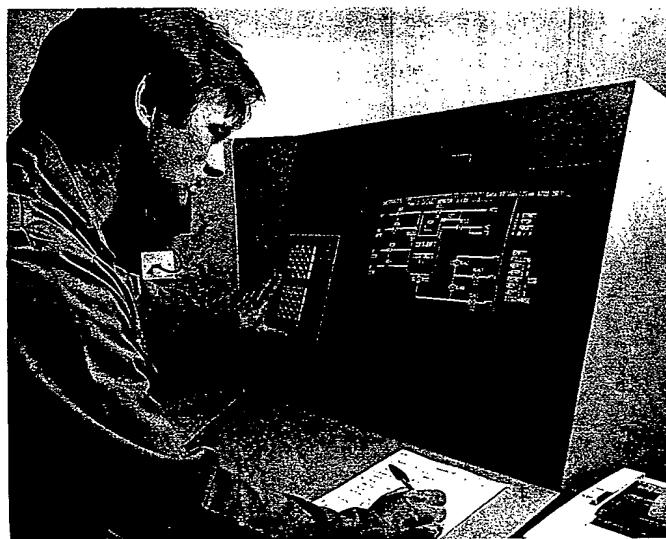
CROSFIELD SOLUBLE SILICATES

THE MANUFACTURE OF SOLUBLE SILICATES

The processes used for the manufacture of soluble silicates, chiefly sodium or potassium, fall into two broad categories, the furnace route and the hydrothermal process.

The furnace or glass method is characterised by the direct fusion of sand and a source of alkali, which is normally in the carbonate form, in an oil or gas fired regenerative furnace at a temperature of about 1400°C. This temperature is needed to achieve a reasonable operating melting rate combined with a viscosity low enough to provide a continuous stream of molten glass through the furnace. The molten glass is very corrosive to refractory materials and great care is required in furnace design. When solid, the glass is dissolved in water under conditions of elevated temperature and pressure to give a range of commercial solutions.

The hydrothermal process depends upon the direct dissolution of sand or another source of pure silica in caustic soda, in nickel lined autoclaves. Modern plant design permits efficient operation and control under the extremely aggressive working conditions involved. Using advanced computer controlled techniques, silicate solutions can be made by this process to extremely fine tolerances for such parameters as silica:alkali ratio and density.



The sand and alkali required for the manufacture of silicates by either process must be of high purity. Typically, commercial silicate solutions contain about 200 parts per million of iron and aluminium (expressed as oxide) with less than about 5 parts per million of other individual heavy metal contaminants. Where specific application conditions impose even stricter purity requirements, for example in the detergent or chemical industries, these can be achieved particularly via the hydrothermal route by careful selection of starting materials and control of process parameters. Finally, modern filtration techniques can be applied to both processes to give brilliantly clear products.

Silicate solution of any silica:alkali ratio can be dried to produce a range of hydrous powders which usually contain 15%–25% moisture, depending upon the operating conditions. The manufacture can be carried out in drum or spray driers or fluid bed conditions to give products with a range of densities, solubilities and particle sizes to suit particular application requirements.

Crystalline metasilicates can be made by the furnace or glass route mentioned previously but modern processes mostly use rotary moving bed techniques or fluid bed driers. Such processes give spherical highly soluble materials which are ideally suited for use in compounded detergent formulations.

The following diagrams illustrate schematically the two principal techniques for the manufacture of alkaline silicate.

CROSFIELD CHEMICALS

THE CROSFIELD RANGE OF SOLUBLE SILICATES

*CROSFIELD CRYSTAL SODIUM SILICATE SOLUTIONS

By far the greatest number of applications of sodium silicate require the material in the form of an aqueous solution. The Crosfield Crystal range includes products having silica to alkali ratios from 1.60:1 to 3.85:1. This range spans the area over which wholly stable sodium silicate solutions can be produced and makes available materials to cover all possible user requirements.

Crystal sodium silicate solutions are manufactured by special processes which result in products of high purity and clarity.

In the Crosfield nomenclature, each product is defined by a number representing its density in degrees Twaddell, along with a qualifying letter designating ratio where appropriate. Typical data for the full range is shown below.

| Grade | Mean Density at 20°C/20°C | | | Mean Wt Ratio SiO ₂ :Na ₂ O | Mean Mol Ratio SiO ₂ :Na ₂ O | Mean Na ₂ O % | Mean SiO ₂ % | Mean Total Solids % | Viscosity at 20°C cP† (mPas) | Litres per Tonne | Gallons per Tonne |
|--------------|---------------------------|------|------|------------------------------------------------------|-------------------------------------------------------|--------------------------|-------------------------|---------------------|------------------------------|------------------|-------------------|
| | °Tw | °Bé | SG | | | | | | | | |
| Crystal 140 | 140.0 | 59.7 | 1.70 | 2.00 | 2.06 | 18.00 | 36.00 | 54.0 | 100,000 | 586 | 129 |
| Crystal 125 | 125.0 | 55.8 | 1.62 | 2.00 | 2.06 | 16.55 | 33.15 | 49.7 | 4,000 | 614 | 135 |
| Crystal 120A | 120.0 | 54.4 | 1.60 | 2.00 | 2.06 | 16.07 | 32.15 | 48.2 | 2,000 | 623 | 137 |
| Crystal 120H | 120.0 | 54.4 | 1.60 | 1.60 | 1.65 | 17.98 | 28.75 | 46.7 | 900 | 623 | 137 |
| Crystal 112 | 112.0 | 52.1 | 1.56 | 2.00 | 2.06 | 15.27 | 30.55 | 45.8 | 800 | 641 | 141 |
| Crystal 106 | 106.0 | 50.2 | 1.53 | 2.70 | 2.79 | 12.45 | 33.60 | 46.1 | 3,000 | 650 | 143 |
| Crystal 100A | 100.0 | 48.3 | 1.50 | 2.00 | 2.06 | 14.03 | 28.05 | 42.1 | 200 | 664 | 146 |
| Crystal 100N | 100.0 | 48.3 | 1.50 | 2.25 | 2.32 | 13.20 | 29.70 | 42.9 | 275 | 664 | 146 |
| Crystal 100S | 100.0 | 48.3 | 1.50 | 2.50 | 2.58 | 12.45 | 31.10 | 43.6 | 400 | 664 | 146 |
| Crystal 96 | 96.0 | 47.0 | 1.48 | 2.85 | 2.94 | 11.20 | 31.95 | 43.2 | 600 | 673 | 148 |
| Crystal 95 | 95.0 | 46.7 | 1.47 | 2.65 | 2.73 | 11.50 | 30.70 | 42.2 | 270 | 673 | 148 |
| Crystal 90S | 90.0 | 45.0 | 1.45 | 2.82 | 2.91 | 10.70 | 30.17 | 40.9 | 200 | 691 | 152 |
| Crystal 84 | 84.5 | 43.1 | 1.42 | 3.20 | 3.30 | 9.45 | 30.25 | 39.7 | 650-1200 | 700 | 154 |
| Crystal 82 | 82.0 | 42.2 | 1.41 | 3.30 | 3.41 | 9.07 | 29.90 | 39.0 | 700-1200 | 709 | 156 |
| Crystal 79 | 79.5 | 41.2 | 1.40 | 3.30 | 3.41 | 8.85 | 29.25 | 38.1 | 250-500 | 714 | 157 |
| Crystal 75 | 75.0 | 39.6 | 1.38 | 3.20 | 3.30 | 8.63 | 27.60 | 36.2 | 100 | 727 | 160 |
| Crystal 74 | 74.0 | 39.2 | 1.37 | 3.37 | 3.48 | 8.25 | 27.90 | 36.2 | 150 | 732 | 161 |
| Crystal 70 | 70.0 | 37.6 | 1.35 | 3.30 | 3.41 | 8.00 | 26.40 | 34.4 | 70 | 741 | 163 |
| Crystal 66 | 66.0 | 36.0 | 1.33 | 3.65 | 3.78 | 7.19 | 26.25 | 33.4 | 200 | 750 | 165 |
| Crystal 52 | 52.5 | 30.2 | 1.26 | 3.85 | 3.97 | 5.75 | 22.20 | 28.0 | 20 | 791 | 174 |

† Unless a range is stated the viscosities here given are average values

*CLAYSIL MODIFIED SODIUM SILICATES

Clay-loaded sodium silicates are available for use as adhesives in paper board lamination, case-sealing and the bonding of insulation materials. These products prevent premature absorption of the sodium silicate by very porous surfaces, the quantity of clay required increasing in relation to the porosity of the surface.

| Grade | Mean Wt Ratio SiO ₂ :Na ₂ O | Mean Mol Ratio SiO ₂ :Na ₂ O | Mean Na ₂ O % | Mean SiO ₂ % | Mean Total Solids % | Viscosity at 20°C cP (mPas) |
|---------------|------------------------------------------------------|-------------------------------------------------------|--------------------------|-------------------------|---------------------|-----------------------------|
| Claysil No. 1 | 3.30 | 3.41 | 6.57 | 21.70 | 48.3 | 250-1200 |
| Claysil No. 5 | 3.30 | 3.41 | 8.30 | 27.39 | 40.7 | 250-1000 |

* 'Crosfield Crystal' and 'Claysil' are trade marks

*PYRAMID SODIUM SILICATE GLASS

Sodium silicate glass is an anhydrous solid, having a low rate of solubility in water under normal conditions.

Pyramid sodium silicate glass is available in two basic compositions. Pyramid AL and AP Alkaline have a 2.00:1 silica to sodium oxide ratio and Pyramid NL and NP Neutral a 3.35:1 ratio.

Both grades are supplied in either lump or powder form.

| Grade | Mean Wt Ratio SiO ₂ :Na ₂ O | Mean Mol Ratio SiO ₂ :Na ₂ O | Mean Na ₂ O % | Mean SiO ₂ % | Physical Form |
|------------|---------------------------------------------------|----------------------------------------------------|--------------------------|-------------------------|---------------|
| Pyramid AL | 2.00 | 2.06 | 33.15 | 66.30 | Lump |
| Pyramid AP | 2.00 | 2.06 | 33.15 | 66.30 | Powder |
| Pyramid NL | 3.35 | 3.46 | 22.90 | 76.72 | Lump |
| Pyramid NP | 3.35 | 3.46 | 22.90 | 76.72 | Powder |

CRYSTAL SOLUBLE POWDERS

Soluble powders are forms of solid sodium silicate which are soluble in water under normal conditions. They are produced by spray-drying sodium silicate solutions in such a way that about 20% water remains in the solid.

Crystal soluble powders are available in two grades as shown below. Crystal C powder has a silica to alkali ratio of 2.00:1 and is soluble in cold water, whereas Crystal M powder, because of its higher ratio of 3.30:1, dissolves more readily at a higher temperature (75°C–80°C).

| Grade | Mean Wt Ratio SiO ₂ :Na ₂ O | Mean Mol Ratio SiO ₂ :Na ₂ O | Mean Na ₂ O % | Mean SiO ₂ % | Mean Total Solids (approx) % | Bulk Density g/Litre |
|-------------------|---------------------------------------------------|----------------------------------------------------|--------------------------|-------------------------|------------------------------|----------------------|
| Crystal C Powder | 2.00 | 2.06 | 27.00 | 53.00 | 80.0 | 400-500 |
| Crystal M Powder | 3.30 | 3.41 | 18.50 | 61.50 | 80.0 | 550-650 |
| Crystal AL Powder | 2.00 | 2.06 | 28.00 | 56.00 | 84.0 | 80-120 |

PYRAMID POTASSIUM SILICATES

The Pyramid range of potassium silicate solutions includes products having silica to alkali ratios ranging from 1.43:1 to 2.48:1. Each product is defined by a number representing its density in degrees Twaddell.

| Grade | Mean Density at 20°C/20°C | | | Mean Wt Ratio SiO ₂ :K ₂ O | Mean Mol Ratio SiO ₂ :K ₂ O | Mean K ₂ O % | Mean SiO ₂ % | Mean Total Solids % | Litres per Tonne | Gallons per Tonne |
|--------------|---------------------------|------|------|--------------------------------------------------|---------------------------------------------------|-------------------------|-------------------------|---------------------|------------------|-------------------|
| | *Tw. | °Bé | SG | | | | | | | |
| Pyramid K120 | 120.0 | 54.4 | 1.60 | 1.43 | 2.24 | 21.60 | 30.80 | 52.4 | 623 | 137 |
| Pyramid K84 | 84.0 | 42.9 | 1.42 | 1.89 | 2.96 | 14.50 | 27.20 | 41.7 | 700 | 154 |
| Pyramid K81 | 81.5 | 42.0 | 1.41 | 2.01 | 3.15 | 13.65 | 27.45 | 41.1 | 704 | 155 |
| Pyramid K78 | 78.5 | 40.9 | 1.39 | 2.09 | 3.27 | 13.00 | 27.10 | 40.1 | 718 | 158 |
| Pyramid K75 | 76.0 | 39.9 | 1.38 | 2.14 | 3.35 | 12.45 | 26.65 | 39.1 | 722 | 159 |
| Pyramid K71 | 71.0 | 38.0 | 1.35 | 2.05 | 3.21 | 12.10 | 24.80 | 36.9 | 741 | 163 |
| Pyramid K66 | 66.0 | 36.0 | 1.33 | 2.05 | 3.21 | 11.40 | 23.35 | 34.8 | 750 | 165 |
| Pyramid K53 | 53.0 | 30.4 | 1.26 | 2.48 | 3.89 | 8.60 | 21.30 | 29.9 | 791 | 174 |
| Pyramid K49 | 49.0 | 28.5 | 1.24 | 2.20 | 3.45 | 8.60 | 18.90 | 27.5 | 804 | 177 |

*'Pyramid' is a trade mark

PHYSICAL AND CHEMICAL PROPERTIES OF SOLUBLE SILICATES

STRUCTURE

The proportions of silica and alkali in soluble silicates are usually expressed on a weight ratio basis with the alkali as M_2O held at unity. For example a sodium silicate solution containing 36.0% SiO_2 and 18.0% Na_2O would be said to have a weight ratio of 2.00:1 the silica usually being expressed first. As the molecular weights of Na_2O and SiO_2 are very similar, there is only a very small difference between the weight ratio and molecular ratio for a particular sodium silicate but this is not so for potassium and lithium silicates.

The molecular ratio is obtained as follows:

Sodium silicate :molecular ratio = $1.032 \times \text{weight ratio}$

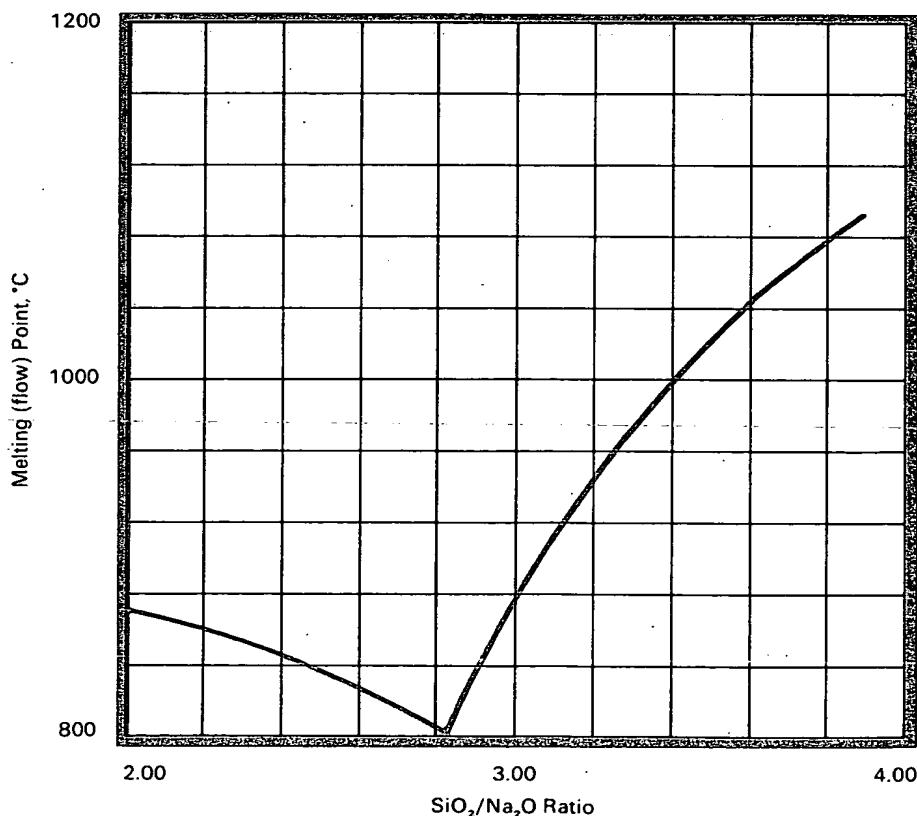
Potassium silicate:molecular ratio = $1.568 \times \text{weight ratio}$

Lithium silicate :molecular ratio = $0.50 \times \text{weight ratio}$

Silicate glasses contain SiO_4 tetrahedra which are common to the many forms of silica, crystalline silicates and glasses. The silicate tetrahedra may be monomers or polymerised with up to four other tetrahedra sharing oxygen-atoms to form Si—O—Si bridges. A situation would never arise however, where two tetrahedra would be joined by more than one oxygen atom.

The overall structure in the glass is a random arrangement of the SiO_4 molecules with sodium ions spaced in the interstices. This structure explains the rather unusual melting point curve in Figure 1 which is obtained for sodium silicate glasses of various ratios. The values given are not true melting points, but rather flow points as it is impossible to measure an accurate melting point. A similar flow point curve can be constructed for potassium silicate which shows higher values than the corresponding sodium silicate—a property utilised in applications such as insulation materials where temperature resistance is important.

FIGURE 1 — THE SOFTENING POINT OF SODIUM SILICATE GLASSES



CROSFIELD CHEMICALS

Soluble silicate solutions contain mixtures of ions, some of very high molecular weight. The type and distribution of the ions depend upon the ratio and concentration of the particular solution. Solutions having a molecular ratio of approximately 2.00:1 or below will tend to be nearer to true solutions containing SiO_4^{4-} and $\text{Si}_2\text{O}_5^{2-}$ ions, usually in a hydrated form. While the higher ratios will contain these same two ions, a large proportion of the silicate will be present as higher polymers. It is believed that an equilibrium situation develops for any given chemical composition of solution, but the time required for the equilibrium to become established after production or change in the solution will depend upon the efficiency of mixing. There is evidence that equilibrium is more easily established with lower ratio ($\text{SiO}_2:\text{M}_2\text{O}$) solutions. In silicates with a ratio of unity or below such as the sodium meta-, and orthosilicates some of the characteristics of true solutions are exhibited.

The sodium and potassium silicates having a molecular ratio exceeding 2.50:1 are generally classed as "neutral" and those with a ratio of less than 2.50:1 are termed "alkaline". These classifications are not strictly speaking correct, however, as all silicate solutions have an alkaline reaction as shown in Tables 1-3.

TABLE 1 — pH VALUES OF VARIOUS SODIUM SILICATES IN THE CRYSTAL RANGE

| Grade | Mean Molecular Ratio $\text{SiO}_2:\text{Na}_2\text{O}$ | Mean Total Solids % | pH of Product | pH of 1% w/w Solution |
|--------------|------------------------------------------------------------|---------------------|---------------|-----------------------|
| Crystal 120H | 1.65 | 46.7 | 13.5 | 11.9 |
| Crystal 125 | 2.06 | 49.7 | 13.2 | 11.7 |
| Crystal 112 | 2.06 | 45.8 | 12.9 | 11.6 |
| Crystal 100A | 2.06 | 42.1 | 12.7 | 11.4 |
| Crystal 100S | 2.58 | 43.6 | 12.3 | 11.2 |
| Crystal 95 | 2.73 | 42.3 | 12.2 | 11.1 |
| Crystal 96 | 2.94 | 43.2 | 12.1 | 11.1 |
| Crystal 84 | 3.30 | 39.7 | 11.8 | 10.9 |
| Crystal 79 | 3.41 | 38.1 | 11.6 | 10.8 |
| Crystal 52 | 3.97 | 28.0 | 10.9 | 10.5 |

TABLE 2 — pH VALUES OF VARIOUS POTASSIUM SILICATES IN THE PYRAMID RANGE

| Grade | Mean Molecular Ratio $\text{SiO}_2:\text{K}_2\text{O}$ | Mean Total Solids % | pH of Product | pH of 1% w/w Solution |
|--------------|-----------------------------------------------------------|---------------------|---------------|-----------------------|
| Pyramid K120 | 2.24 | 52.4 | 12.6 | 11.5 |
| Pyramid K66 | 3.21 | 34.8 | 11.8 | 10.9 |
| Pyramid K53 | 3.89 | 29.9 | 10.9 | 10.5 |

TABLE 3 — pH VALUES OF SODIUM META — AND ORTHOSILICATES

| Grade | Mean Molecular Ratio $\text{SiO}_2:\text{Na}_2\text{O}$ | Mean Total Solids % | pH of 10% w/w Solution | pH of 1% w/w Solution |
|--------------------------------------------|------------------------------------------------------------|---------------------|------------------------|-----------------------|
| Metso Sodium Metasilicate Pentahydrate | 1:1 | 57.0 | 13.0 | 12.3 |
| Metso Sodium Metasilicate Anhydrous | 1:1 | 100 | 13.2 | 12.5 |
| Acsil O Sodium Orthosilicate | 1:2 | 63.0 | 13.4 | 12.8 |
| Acsil OC Sodium Orthosilicate Concentrated | 1:2 | 89.0 | 13.5 | 12.9 |

The stability of silicate solutions depends to a large extent on pH and a silica hydrogel will be formed whenever the pH of sodium silicate solution is reduced below about 10. The actual time required to form the gel depends on several factors, the most important being pH and concentration of the solution.

CHAPTER 4

Colloidal Silica-Concentrated Sols

DEFINITION OF COLLOIDAL SILICA AND HISTORICAL DEVELOPMENT

The term "colloidal silica" here refers to stable dispersions or sols of discrete particles of amorphous silica. By arbitrary definition, the term excludes solutions of polysilicic acid in which the polymer molecules or particles are so small that they are not stable. Such solutions, which are usually obtained by acidifying sodium silicate solutions or by hydrolyzing silicon esters or halides at ordinary temperatures, have been discussed in Chapter 3 as precursors of colloidal particles.

Stable concentrated silica sols that do not gel or settle out for at least several years became available in the 1940s, after it was learned how to make uniform colloidal particles larger than about 5 nm in diameter, stabilized with an optimum amount of base.

When Vail (1) in 1925 and Treadwell and Wieland (2) in 1930 reviewed the status of colloidal silica, only rarely could a silica sol containing more than 10% silica be obtained; such sols were not stable toward gelling. In 1933 the art was reviewed by Griesbach (3), who reported that a 10% sol stabilized with ammonia was made by I. G. Farbenindustries, A.G. In 1941 Bird (4) patented a process for removing the alkali from a dilute solution of sodium silicate by a hydrogen ion-exchange resin, adding back a small amount of alkali to stabilize the silica, and concentrating by heating to boil off water. It is now evident that under these conditions silica particles were grown to 5–10 nm in diameter. In 1945, White (5) patented a process of washing the salts out of silica gel made by acidifying a solution of sodium silicate, impregnating it with an alkaline solution, and then heating until most of the gel is peptized to a sol. These processes generally gave sols containing 15–20% silica, at least temporarily stabilized against gelling or settling out. In 1951 Bechtold and Snyder (6) developed the first process for making colloidal silica particles of uniform and controlled size, and Rule (7) further defined the optimum concentrations of alkali required for stabilization while limiting electrolyte impurities.

The history of the development and the state of the art in about 1954 was summarized by Iller (8). Further refinements by Alexander (9) in controlling particle size,

degree of aggregation, purity, and optimum concentration of stabilizing alkali led to stable sols of particles only 8 nm in diameter, yet containing more than 30% silica. Stable, translucent, aqueous sols containing up to 50% by weight of SiO_2 , have been developed (10, 11) by making particles 20–25 nm in diameter and adding an optimum amount of alkali for stabilization and sufficient salt to reduce the viscosity without destroying stability.

Sols containing discrete particles as large as 300 nm or more in diameter, which settle out on standing, have been made by autoclaving wet silica gel with a base apart in a colloid mill (12a).

Thus in the past 30 years methods have been developed for making discrete silica particles covering the whole range of colloidal size and stabilizing these as concentrated commercial sols.

A broad review of "hydrosols" has been written by Napper and Hunter, including their preparation and properties (12b).

GROWTH AND STABILIZATION OF DISCRETE PARTICLES

As discussed in Chapter 3 (see Figure 3.1) silicic acid polymerizes to form discrete particles in the pH range 7–10. No aggregation occurs if the concentration of electrolyte is generally less than 0.1–0.2 N, depending on silica concentration.

Because of the nonuniform distribution of particle-sizes, especially when particles are smaller than 10 nm, spontaneous particle growth occurs. The particle size that is attained strongly depends on the temperature. As shown in Table 3.5, at 50–100°C particles reach 4–8 nm in diameter, whereas at 350°C in an autoclave they may grow to 150 nm. This spontaneous growth is relatively independent of the silica concentration. The size of particles produced by autoclaving aqueous sols is limited at high temperature by the conversion of amorphous silica to crystalline quartz. Fyre and McKay have shown that the rate of conversion under autogenous pressure at 330°C is proportional to the square of the hydroxyl ion concentration (13). Oehler (14) reported that after 4 weeks at 150°C and 2000 bars microspheres of crystalline triydymite 50 microns in diameter were formed.

Increasing Particle Size By Adding "Active" Silica

It was because of the small particle size of the colloidal silica made at ordinary temperature that stable concentrated sols could not be obtained. Because higher temperature was known to accelerate gelling, it seemed logical that sols should be made and kept at ordinary temperature. Hence the ultimate particle size seldom exceeded 2–3 nm. When a sol of this type was adjusted to pH 8–10 and vacuum concentrated at 20–30°C it gelled when the concentration reached about 10%. It was not realized that it could be heated and evaporated at 100°C to a stable concentration of 10–20% because at the higher temperature the particle size increased to 4–6 nm.

in turn, into even larger ones have been described by Greer (71). Stages of particle sizes 1.5, 10, 60, and 331 nm were described and an equation was given:

$$d = ar^{n-1}$$

where d is the diameter of the sphere at stage growth n , a is the diameter of the units of the initial growth stage, and r has a value of 6. If one assumes that a is 1.5 nm, then the stages should occur at 9, 54, and 324 nm. Conditions for bringing about such aggregation were not disclosed.

Microporosity in colloidal particles may in some cases be demonstrated by low angle X-ray diffraction. When the particle size determined in this way is much smaller than the size calculated from the specific surface area by nitrogen adsorption or observed in electron micrographs it means that the particles are made up of still smaller discrete units so closely packed that the pores are not large enough to be penetrated by nitrogen molecules (72). Most silica gels consist of primary particles with intervening pores accessible to nitrogen. However, Ledderer, Schurz, and Janzon (73) reported that particles in their particular silica gels appeared to have some "inner" area, because hydration corresponded to 0.15-0.26 gram H₂O per gram of silica, which would indicate a high porosity.

Elongated Particles

An astounding observation of elongated or spindle-shaped silica particles has been reported by Ogino and Kuronuma (74). This is the first time that discrete silica particles of colloidal size have been observed with a shape other than spherical. They were formed by adding hydrogen ion-exchange resin slowly to a dilute solution of sodium silicate (3.52 SO₄) at 40°C until the pH dropped to 3, then adding ammonia to raise the pH to 8-9 and heating 1 hr at 80°C.

Particles With Non-Siliceous Cores

As long as the surface of a colloidal particle consists of silica, its colloid properties are the same as those of solid silica particles. As discussed in chapter 1, silica can be deposited on a wide variety of surfaces, as shown by Iler (18). To coat sol particles carrying a positive charge, like Fe₂O₃ or Al₂O₃, it is first necessary to reverse the charge by adding the dilute sol into a dilute (10%) solution of sodium silicate under conditions of intense agitation. It is also possible to reverse the charge with a chelating agent such as citrate before adding silicate. The surface is thus covered with a negatively charged molecular layer of adsorbed silicate on which a layer of SiO₂ can be applied. A sol of silica-clad thorium particles has been made by Barrett, Moises, and Vanik (75). Stable sols of particles greater than 50 nm in diameter contained up to 60% solids. The silica coating was about 50% by weight of the thorium core. Silica-coated particles of thorium and urania are claimed by Fitch, Sanchez, and Vanik (76). The kinetics of absorption of silica onto the surface of particles of thorium was determined at 100-200°C in an autoclave (77).

METHODS OF MAKING SOLS

Many processes have been proposed and are employed for producing colloidal silica from low-cost sodium silicate solutions. Sols have also been made from hydrolyzable compounds such as ethyl silicate or silicon tetrachloride. To produce sols that are stable at a reasonably high concentration, it is necessary to grow the particles to a certain size under alkaline conditions where the particles remain negatively charged so they will not flocculate or gel. The particles should also be nonporous.

Colloidal silica is formed in nature when water is saturated with quartz at high temperature and pressure and the solution is removed and cooled. Such sols contain only a few tenths of a percent silica, but could be concentrated readily by ultrafiltration. The formation of colloidal silica in this manner was studied by Kitahara and Oshima (78), who also examined the rate of dissolution of the particles when the sol was diluted.

Neutralizing Soluble Silicates With Acids

When a dilute solution of sodium silicate is partially neutralized with acid to a pH of 8-9, a silica sol rather than a gel is obtained if the concentration of the resulting sodium salt is less than about 0.3 N, and if the neutralization is carried out at elevated temperature, so that the particles grow as soon as they are formed to several millimicrons in size. Thus a 3% silica sol may be made by partially neutralizing a dilute solution of commercial silicate with acid, according to the conditions patented by Alexander, Iler, and Wolter (79). A sol of silica nuclei is first made by removing sodium ion with an ion-exchange resin from a sodium silicate solution containing 2.2% SiO₂, until the weight ratio of SiO₂ to Na₂O is 85:1. This dilute sol is then heated at 100°C for about 10 min to form nuclei of desired size. Then dilute solutions of sodium silicate and sulfuric acid are added simultaneously while the mixture is stirred vigorously at 95°C over a period of 8 hr and the pH is maintained at about 9. The concentration of sodium ions must not exceed about 0.3 N or aggregation of the particles will occur. Under these conditions, the silicic acid formed by the added silicate and acid is deposited upon the silica nuclei, so that particles of 37 nm size, for example, are obtained.

In another patent, Alexander and Iler (80) describe the isolation of particles formed in the above process by coagulating them with a metal ion such as calcium, washing the precipitate free from sodium salt, and then peptizing the product to a more concentrated silica sol by removing the calcium ions by ion exchange, for example.

In making a sol by neutralizing a dilute solution of silicate with acid, it is essential that the mixing be carried out so rapidly that none of the mixture remains in the pH range of 5-6 for an appreciable time, since silicic acid gels almost instantly at this pH. This requires that the acid and silicate be mixed with intense turbulence, with either excess acid or excess silicate present to prevent local gelling. Even in the most critical pH region, around neutrality, a mixing procedure patented by Armstrong and Cummings (81) permits the formation of a uniform silicic acid solution at

does not gel for a few minutes.

A different approach to making colloidal silica by reacting sodium silicate with acid involves making an acidic sol and precipitating the sodium salt in a strongly acidic medium. The polysilicic acid is temporarily stable at pH 2, and if the sodium salt of the acid used for neutralizing the silicate is sufficiently insoluble, it can be precipitated and separated. Once the sodium salt is separated from the acid sol, the polysilicic acid can be alkalinized to grow colloidal particles and stabilize the product, or can presumably be used for other processes of growing silica particles to the desired size. Thus Teicher (82) neutralized sodium silicate with an acid to produce an acidic sol containing a miscible organic liquid, such as an alcohol, which precipitates the salt. An earlier process by White (83) precipitates the sodium sulfate from a sol made from sodium silicate and sulfuric acid by adding acetone. Mar-chegut and Gandon (84) instead use a material that will form an extremely insoluble sodium salt, such as the reaction product of sulfite ion and glyoxal, the sulfite being the acid used for neutralizing the alkali in the silicate. By reacting sodium silicate with oxalic acid to obtain an acidic sol, sodium is precipitated as sodium hydrogen oxalate, leaving about 0.13 N sodium ion in solution at 15°C (85). The remaining salt can then be removed by ion exchange (86).

Electrodialysis

Colloidal silica has been made by various procedures involving electrodialysis whereby sodium ions are removed from a solution of sodium silicate to produce sol. These have been reviewed by Iler (8), but in no case were stable products made. Sanchez (87) and Iler (88) patented processes of electrolyzing alkali metal silicate solution to continuously remove alkali metal ions until a sol is obtained.

Electrodialysis may eventually replace ion exchange for making commercial sols because alkali, oxygen, and hydrogen could be recovered and there is much less waste water containing salts to be disposed of. In the Iler process, there are three compartments. In the anode compartment sulfuric acid solution is circulated around a lead anode and in the cathode compartment where sodium hydroxide is generated, the alkali is circulated around the steel cathode. These are located on opposite sides of two parallel, closely spaced cation-exchange membranes between which the process solution is rapidly circulated at 60–90°C. The process solution is a silica sol containing about 0.05 N Na₂SO₄ as a conducting or supporting electrolyte. A solution of sodium silicate is added to the entering process stream to raise the pH to 9.5. The current density and rate of flow of the process stream are adjusted so as to reduce the pH to no less than 8 as the stream leaves the cell. The liberated silica is deposited on the silica particles which are thus grown to desired size. A 25% silica sol of 15 nm particles can be prepared directly by this process. The electrolyte is then removed by ion exchange, the pH adjusted for optimum sol stability, and the sol concentrated to 30–50% silica.

There is essentially no consumption of acid except the small amount needed at the start of each batch to neutralize a dilute solution of sodium silicate (0.5% SiO₂) to pH 9 at 60–90°C to form silica nuclei to start the process. A narrow uniform spac-

ing between the membranes is required. Water is added to the anode compartment since it is slowly transported to the cathode compartment, from which sodium hydroxide solution is constantly withdrawn. Anolyte and catholyte are circulated from the corresponding electrode compartments to separators for the removal of oxygen and hydrogen gases.

A process using a mercury cathode to remove sodium from sodium silicate is patented by Vaquero (89). No supporting electrolyte is used so that as the alkali becomes depleted the high electrical resistance of the sol increases the power required. A three cell arrangement using ion-exchange membranes for making sols by electrodialysis was discussed by Prajapati and Taipade (90). No supporting electrolyte was used. The final sol pH was 2–3.

A type of electrolytic process patented by Tripp (91) is used to dissolve an anode of silicon metal in alcohol containing a metal salt catalyst such as copper sulfate to produce a silica organosol.

In a study of transport of silica through membranes during electrodialysis, Boari et al. (92) found that no transport or silica deposition occurred unless the pH was such that HSiO₃⁻ ions were present. This is consistent with the observation that it is necessary to carry out electrodialysis at less than pH 9.5 (88) in order not to deposit silica in the membrane.

Ion Exchange

The pioneering work of Bird (4) by which sodium was removed from sodium silicate by ion exchange, after which the sol was concentrated by evaporation at atmospheric pressure, led to one of the earliest stable silica sols containing around 20% silica. Further advances by Bechtold and Snyder (6) permitted control of particle size, and other modifications, relating to permissible salt concentration and optimum alkali content, by Alexander (9) and Atkins (10) led to the production of a series of concentrated sols covering a wide range of particle sizes. Thus far, the silica sols were made by passing relatively dilute sodium silicate solution through a bed of ion-exchange resin to produce an acidic sol relatively free from sodium, which was then stabilized and the particles grown as desired. An alternative approach was invented by Wolter and Iler (93), in which the hydrogen ion-exchange resin and sodium silicate were added to a weakly alkaline aqueous reaction medium in the pH range around 9, at elevated temperature. The silica particles grew continuously under these conditions where they were stabilized against aggregation, so that relatively concentrated sols in the range 10–15% silica were produced directly. An alternative procedure for making a relatively concentrated 12% acidic sol of polysilicic acid has been patented by Mindick and Reven (94), whereby the silicate solution is cooled and passed through an ion exchanger so that the concentrated sol is formed at low temperature to avoid gelling.

Many variations in the ion-exchange procedure have been proposed. Dirlberger (95) showed that more concentrated sols can be made without gelling by passing the silicate solution upward through the ion-exchange resin bed, keeping the resin in suspension. Other variations in the ion-exchange process have also been patented (96).

The last trace of electrolytes can be removed from silica sol produced by conventional means by heating and again passing it through a hydrogen ion resin to remove alkali liberated from the particles, according to Mindick and Reven (65).

The use of a cation-exchange resin in ammonium form permits removal of sodium from sodium silicate solution without exposing any part of the solution to low pH where aggregation can occur. Wolter found that a 3:25 ratio silicate solution containing up to 6% SiO_2 , could be passed through a column of ammonium resin without gelling. More silicate can be added to the alkaline effluent and the solution again treated with ammonium resin (97).

For sols of very small particle size, Shannon (98) added sodium silicate to an acidic suspension of resin until the silica concentration reached 8%. The sol was removed and alkalinized with NaOH and NH_3 to have 1% Na and 3% NH_3 , based on the SiO_2 .

When making silicic acid by passing a solution of sodium silicate containing more than 3-4% SiO_2 , through a bed of hydrogen ion-exchange resin, silica gel is formed within the pores of the conventional resin. This not only results in a loss of silica and the need to clean the bed, but also causes the resin granules to disintegrate. According to Hoffman (99) a silicic acid effluent containing up to 6% SiO_2 , can be made without these difficulties if one uses a macroreticular cation-exchange resin (Amerlite IR-200) having pores about 10 nm in diameter, a porosity of 32%, and a surface area by nitrogen adsorption of $42 \text{ m}^2 \text{ g}^{-1}$. The resin is treated with caustic solution to remove small amounts of silica after each use and before regeneration.

Ion exchangers can be regenerated electrolytically according to Matejka (100). Instead of an ion-exchange resin, a cation-exchange membrane can be used to remove sodium from a silicate solution into sulfuric acid (101). A hot sol of nuclei particles is circulated rapidly through tubing of ion-exchange polymer which is immersed in dilute sulfuric acid. Sodium silicate is added to the sol at a rate to maintain the pH around 8-10 and the liberated silica is deposited on the sol particles, thus increasing their size. Some sulfate ions penetrate the membrane so that the concentration of sodium sulfate in the sol slowly increases with time. The sol can be purified and concentrated by ultrafiltration, but the sol concentration must be maintained so that the sodium in normality N does not exceed $N = 0.26 - 0.005C - 0.0012(T - 40)$, where C is grams of SiO_2 per 100 ml and T is the temperature in degrees centigrade.

Peptizing Gels

As early as 1864, Thomas Graham reported that silica gel could be liquefied by a trace of alkali, which he described as "peptization of the jelly." In 1922, Praetorius and Wolf (102) produced silica sol from a gel by heating it in water at elevated temperature and pressure. Neundlinger (103) prepared sols containing about 10% silica by treating the gel first with ammonia and heating without evaporating water until a sol was produced. Improved similar processes were invented by White (5) and Trail (104).

Hydrolysis of Silicon Compounds

In 1944, Radczewski and Richter (67) reported that very pure silica sols prepared by hydrolyzing silicon tetrachloride from which the acid has been removed to give a pH of 6.8 formed spherical particles up to 200 nm in diameter, and that these appeared to be spongelike under the electron microscope. More recently, Stöber and Fink (68) discovered that very uniform spherical silica particles of almost any desired size up to 1 micron could be made by hydrolyzing a lower alkyl silicate in an alcohol medium containing suitable amounts of water and ammonia. Subsequently, Flachsbart and Stöber (109, 110) were able to incorporate certain radioactive tracers without affecting the growth of the silica particles during their formation, but it was not certain whether the metals were homogeneously incorporated throughout the spheres. Particle sizes from 50 to 900 nm in diameter were produced. It is likely that the large spherical particles are actually spherical aggregates of much smaller particles, 10 nm or less in size, as described by Radczewski.

According to Brinsmead and Brown (111) a "silicic acid sol" containing 43% SiO_2 was made by refluxing a mixture of ethyl silicate and isopropyl alcohol to which a dilute aqueous solution of acid was slowly added to furnish a stoichiometric amount of water for hydrolysis. There was no evidence that hydrolysis was complete, as would be shown by complete miscibility with water, nor any indication that discrete silica particles had been formed.

Sodium silicate can be hydrolyzed if sufficiently diluted. Thus a dilute solution of high ratio sodium silicate can be hydrolyzed in an autoclave to form colloidal particles which coagulate to a precipitate if the sodium ion concentration is sufficiently high. Schnürich and Köster (112) report that when a solution of sodium silicate with a $\text{SiO}_2:\text{Na}_2\text{O}$ weight ratio of 3.89:1 is diluted to 20 g 1^{-1} of SiO_2 and heated 1.5 hr at 150°C, 38% of the silica is precipitated as fine silica.

Dissolution of Elemental Silicon

If pulverized silicon metal is first treated to remove the oxide film with hydrofluoric acid, it reacts rapidly with water in an alkaline medium, particularly ammonia, to

A modification of the preparation of silica sols was reported by Simpson (105), who formed the gel under alkaline conditions by incompletely neutralizing the alkali of a silicate such as sodium silicate with less than the equivalent acid, then washing out the salts and heating the wet gel to peptize it. Much higher conversion of gel to sol is claimed than when an acidic gel is first made. Characteristics of sols made by this process are not available, but probably sols 15-45 nm in diameter were produced. A similar process had been described by Legal (106). Conversion of gel to sol in an autoclave to obtain a 30% ammonia-stabilized sol was patented by Mertz (107). The effect of ultrasonic dispersion of silica gel was examined by Bubyreva and Bindas (108).

form colloidal silica which is stabilized by the alkali. This type of process has been patented by Balthis (69); the process is accelerated by carrying out the reaction while grinding the silicon (113).

Sols made from elemental silicon range from 8 to 35 nm in diameter, and under some conditions up to 150 nm. The process and the nature of the product has been discussed under the heading of "porous particles."

To make sols containing up to 50% SiO_2 by dissolving silicon, Bobb (114) claims the use of an aqueous solution of an inorganic base (NaOH , KOH) to catalyze the dissolution at 50–100°C and stabilize the resulting sol. It is remarkable that sols made at 90–95°C were said to be very viscous but when made at 98–100°C were of normal low viscosity. Particle sizes were between 15 and 45 nm. Also the sols were unusual in that they did not form hard gels when acidified, but only soft coacervates. These differences are unexplained. An alcisol is obtained when silicon is used as an anode and dissolved by electrolysis in an alcohol–water mixture. Acid or a metal salt is added to provide conductivity according to Tripp (91) or Chilton (115).

Dispersion of Pyrogenic Silica

Silica vaporizes only at very high temperature, around 2000°C, but if a reducing agent is present so as to form silicon monoxide, SiO , the sublimation temperature is 1700°C. As the monoxide evaporates in an oxidizing atmosphere, the dioxide is condensed in an extremely finely divided form. Ethyl silicate can be oxidized and the resulting SiO_2 vapor condensed. The most common process involves the combustion of silicon tetrachloride with natural gas, forming hydrogen chloride and silicon dioxide vapor, which condenses to a very voluminous powder. By controlling combustion conditions, presumably in a manner similar to that employed in making carbon black, products of different ultimate particle sizes and degrees of coalescence of the particles can be made. Another process involves vaporizing silica in an electric arc and condensing the resulting vapors. Powders of this type are considered here only because colloidal dispersions can be made from some of them. The processes involved and the silica powders are discussed in Chapter 5.

Dispersion of silica to a sol of separate, discrete, ultimate particles is difficult because the particles are coalesced to varying degrees. Also in many cases, the surface is partly anhydrous with only a few hydrophilic silanol groups. For these reasons the properties of sols of this type are generally different from those made in aqueous solution. They do not form strong gels and are of little use as an inorganic binder.

The patent literature suggests that intense mechanical shearing forces, both on the dry voluminous powder and on the subsequent suspension in water, are required to attain reasonable dispersion in water or polar organic liquids. In water, wetting agents are used to promote wetting of the hydrophilic siloxane surface areas and alkali to promote surface hydration and dispersion (116, 117).

A more stable dispersion is obtained by adding to the silicon tetrachloride a certain amount of titanium or aluminum chloride to produce silica containing a

small amount of the metal oxide. Very stable concentrated suspensions of solids are obtained (118). A silica produced by flame hydrolysis by Degussa, for example, containing 1.3% aluminum oxide based on the silica (Aerosil® MOX), is sold particularly for making concentrated aqueous dispersions with ultimate particles in the range of 20–40 nm diameter, along with many smaller ones (119).

Flame-hydrolyzed silica with specific surface areas in the range of 200–400 $\text{m}^2 \text{g}^{-1}$, under the name of Cab-O-Sil®, is dispersible in water at pH 9 with ammonia, for example, to give sols up to 30% by weight of silica, provided the material is passed through a homogenizer to break apart the three-dimensional network of ultimate particles. The resulting particles still consist mainly of chainlike aggregates which increase the viscosity (120).

In general, the "fume" or "flame hydrolysis" process does not yield silica that is dispersible in water to give sols of discrete particles with the low viscosity at high concentration that is characteristic of sols made by aqueous polymerization processes. Nevertheless, with enough processing, pyrogenic silicas of ultimate particle size of 10–25 nm can be disaggregated and dispersed to aquasols containing up to 40% silica with suitable mechanical treatment and dispersing agents.

Extremely finely divided silica, composed of particles only 25–50 Å in size and having a specific surface area as high as 1000 $\text{m}^2 \text{g}^{-1}$ has been made, according to Spencer, Smith, and Cosman (121), by treating moist carbon black with dimethylchlorosilane and then burning away the organic material in air at 500°C. The resulting silica, amounting to 4% of the original weight of the carbon black, was an opalescent powder in the form of small spheres, about 1 mm in diameter, of about the same size as the carbon black pellets. The specific surface area of the silica was 1094 $\text{m}^2 \text{g}^{-1}$, indicating an ultimate particle size of 2.5 nm. The material dispersed easily in water, with the particles forming chains up to 20 microns long, suggesting that they were partially hydrophobic.

Colloid milling of pyrogenic silica in water in the presence of boric acid or alkali borate is disclosed by Clapdale and Syracuse (122). A 30% sol can be prepared. Some additional patents on making sols from pyrogenic silica mainly involve the use of alkali stabilization with sodium silicate, sodium hydroxide, hydrazine, hydroxylamine, or mixtures with pyrogenic metal oxides (123–125).

PURIFICATION, CONCENTRATION, PRESERVATIVES

Sols made by some processes contain salts or other materials that must be reduced or removed before the sol is finally concentrated.

Ion Exchange

Special purification procedures to remove salts from the final concentrated sols usually involve treatment with ion-exchange resins to remove soluble salts and then stabilization with a minimum of base, including ammonia, to obtain a sol of

CHARACTERIZING SOLS

It was only after methods were developed for following the polymerization of silica, measuring the size of the particles, and defining their degree of aggregation, that enough was learned about the behavior of colloidal silica to control the particle size and predict behavior during processing. An understanding of the surface chemistry of silica and the nature of the interaction between silica and water over a wide pH range was necessary to achieve stabilization and particle growth without aggregation and subsequent particle growth.

The most important characteristics of a silica sol are as follows:

Chemical analysis. Silica, stabilizing base, carbon including carbon dioxide, organic carbon, soluble salts of alkali metals, total solids and non-siliceous ash, metals including aluminum and iron.

Particle characteristics. Size and size distribution, porosity, degree of aggregation, specific surface area, rate of dissolution.

Physical characteristics. pH, density, viscosity, turbidity, refractive index, light scattering, sedimentation rate by ultracentrifugation.

Chemical Analysis

Silica content can be estimated approximately from density or refractive index or determined by conventional analytical procedures (see Chapter 1). The amount of stabilizing base is determined by titrations to a pH of about 3.5, or to 2.0 and correcting for the $10^{-2} N$ acid that is present. The old procedure for "non-siliceous ash," which involved drying and heating the sample in a platinum dish, weighing the residues, fuming off the silica with $\text{HF} + \text{H}_2\text{SO}_4$, and again weighing, is still a useful technique. This leaves a residue in which other elements can be easily determined by atomic absorption. The weight loss is silica.

Aluminum is of special interest because its presence indicates that the surface may be modified with aluminosilicate groups which affect colloid behavior. Aluminum on the silica surface can be determined by extracting the dried silica with hydrogen chloride and analyzing for aluminum. The carbonate and organic matter are important in that carbonate acts as an added electrolyte and may require a correction of the titration of base, and organic matter (usually due to low polymer extracted from ion-exchange resin) can affect product behavior in some applications. Analysis for total nitrogen and carbon reveals the possible presence of organic bases. Particle characteristics are in some cases measured directly and in others inferred from physical characteristics of the sol such as viscosity, turbidity, light scattering, and sedimentation rate.

Measuring pH

The pH of a silica sol is one of its most important characteristics. Sol behavior may vary greatly with only minor change in pH. For example, increasing the pH of only

half a unit will double the rate of gelling at pH 4, or convert a sol to a solution of sodium silicate at pH 10.5.

Measurements are ordinarily made with conventional alkali-resistant glass electrodes, although those specified for solutions high in sodium should be used when measuring the pH in the presence of salt as in titrating specific surface area.

Bolt (140) pointed out that for greatest precision, pH measurements, particularly in concentrated sols, require the use of a "gel bridge" to overcome the "sol concentration effect" on the reference electrode.

Electrolyte Concentration

A reasonably accurate indication of the salt content of a sol, without resorting to chemical analysis, is to measure the electrical conductivity at about pH 4.5. At this pH, the charge on the silica particles is negligible and conductivity is due chiefly to the salt present. When an alkali-stabilized sol is involved, it is titrated with standard acid to pH 4.5 and the resultant sodium salt subtracted from the total salt concentration calculated from the conductivity. Alexander (9) gives the empirical equation

$$N = 8(L - 4.3 \times 10^{-6})$$

where L is the specific conductance of the sol diluted to 4% SiO_2 at 25°C and N is the normality of equivalent Na_2SO_4 .

Particle Characteristics

Particle Size

If the silica content of the sol is more than 10–15% the order of magnitude of the particle size can be judged visually by the turbidity. If the particles are smaller than about 7 nm in diameter the sol is almost as clear as water; from 10 to 30 nm there is a characteristic opalescence or translucency when seen in bulk; above about 50 nm, the appearance is white and milky. Particles larger than 100 nm settle on standing, leaving a transparent upper layer after a few weeks or days.

A review of methods available for fine-particle characterization has been presented by Kuhn (141).

ELECTRON MICROSCOPY. The electron microscope provides a direct method for determining dimensions of colloidal particles (Figure 4.7). With improved equipment, individual particles as small as only 1–2 nm can be discerned, but measuring the diameter of particles smaller than 5 nm is difficult. Alexander and Iler (142) first demonstrated that the particle size of colloidal silica measured by the electron microscope correlated well with particle size determined by light scattering in solution, and also with the size calculated from the specific surface area of the dried silica powder.

The specific surface area calculated from d_s , assuming that the particles are dense, is indicated by the symbol A_d .

An excellent discussion of the definition of particle size has been given by Bailey, Beattie, and Booth (146), and a more recent and broader discussion of particle size and shape is given by Underwood (147).

The particle size distribution in a commerical colloidal silica (Ludox®) has been determined by electron microscopy by Deželić et al. (148). A weight-average diameter, d_w , determined from the particle size distribution curve by electron microscopy, was 20.0 nm, for example, which agreed within the 5% limit of experimental error with the particle diameters calculated from light-scattering data.

A uniformity index, defined as the quotient of the number-average particle diameter divided by the weight-average particle diameter, may be determined by methods described by Bailey, Beattie, and Booth (146).

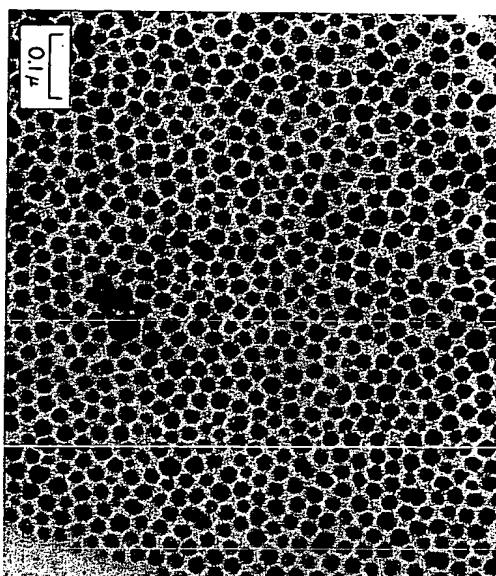


Figure 4.7. Particles of colloidal silica about 20 nm in diameter.

Practically no sols are monodispersed, since the particles usually vary by at least a few millimicrons in diameter. There are several ways of expressing the average particle size. For example, the number-average particle diameter, d_n , is simply the average diameter of a large number of particles. On the other hand, the size can be expressed in terms of a particle which has the same weight as the average weight of the particles, that is, the weight-average diameter, d_w . Likewise, the diameter may be expressed as the diameter, d_s , of a particle which has a surface area equal to that of the average surface area of the particles.

The method of measuring and calculating d_n and d_s has been outlined in a patent issued to Balthis (69), following the method described by Watson (143).

To distinguish discrete particles from permanent aggregates requires that the sol be diluted so much that when the suspension dries, aggregation will not occur on the grid. Greene et al. (144) describe the use of a positively charged layer of cytochrome C on a carbon-coated grid to adsorb negative particles.

For silica, a fresh 0.1% solution of bovine albumin at pH 3 can be used, allowing a thin film to dry on the carbon-coated screen. A drop of sample containing 0.1% SiO_2 is applied and *immediately* rinsed off, leaving a representative population of adsorbed particles and aggregates, after which the screen is dried in air for examination.

Perloff et al. (145) increase the contrast of silica particles by applying a 1% solution of uranium acetate at pH 4.6 and rinsing off the excess.

The specific surface area, S_c , expressed as square meters per gram, may be calculated from d_s in millimicrons, taking the density of silica as 2.2 g cm^{-3} , which is the density of amorphous, anhydrous, nonporous silica, as follows:

$$A_d = \frac{6 \times 10^3}{\text{density} \times d_s} = \frac{2720}{d_s}$$

LIGHT SCATTERING. A series of sols produced by Bechtold and Snyder (6) were characterized by Alexander and Iler (142) by light scattering and the results correlated with particle size determined from electron micrographs. If it is assumed that the silica consists of uniform spheres of density 2.2 g cm^{-3} and number-average diameter, d_n nm, then the theoretical molecular weight, M , in millions, is given by the relation

$$\log d_n = 0.333 \log M + 1.054$$

However, a plot of actual $\log d_w$ versus $\log M$ was best represented by the equation

$$\log d_w = 0.27 \log M + 1.15$$

The disagreement may be due to differences in the distribution of particle sizes since among these samples the ratio of the weight-average particle diameter to the number-average diameter varied from 1.13 to 1.35.

Ludox® colloidal silica, supplied as a sol of 15 nm particles with a molecular weight of about 2.5×10^6 , was used as a standard for the calibration of light-scattering photometers by Maron and Lou (149), who proposed an improved technique for the calibration procedure. At about the same time, Trap and Hermans (150) used Ludox® for calibrating scattering apparatus, having measured the absolute turbidity by transmission measurements. Later Goring et al. (151) reported some difficulty with reproducibility using different samples of colloidal silicas as standards, and also found that erratic results were obtained when samples were diluted with distilled water instead of a dilute salt solution. The latter phenomenon was further investigated by Deželić and Kratochvíl (152), who had noted the same phenomenon (148, 153) in an investigation of the change in the second virial coefficient with electrolyte concentration. They verified that the light-scattering results were much more reproducible in the presence of at least 0.025 M NaCl solution. Greenberg, Chang, and Jarniowski (154) recommended that light-scattering measurements be made in salt solution with an ionic strength of 0.1 in order to suppress the influence of surface charges.

Jennings and Jerrard (155) made a detailed comparison of the particle sizes of two commercial silica sols by light-scattering electron microscopy and ultracentrifugation.

The effect of varying the refractive index of the liquid phase in colloidal silica on light scattering has been studied by Bonnellycke and Dandliker (156), who found that colloidal silica particles themselves do not absorb light by changing the refractive index of the liquid phase, and showed that excess turbidity and scattering go to zero concomitantly.

Claesson and Ohman (157) described an automatic recording light-scattering instrument which was standardized with colloidal silica.

TURBIDITY, ABSORBANCE. As light is scattered, the transmitted light is diminished as it passes through a sol. Transmittance and absorbance are related by the equation

$$A = \log_{10} \frac{100}{T}$$

where A is absorbance and T is percent transmittance, defined as $T = 100I_0/I$, where I_0 is intensity of the incident light and I of the emerging light. As shown in Figure 4.8a at low silica concentrations absorbance is proportional to silica concentration and increases with particle size.

Absorbance using 400 nm wavelength light as in the figure does not provide a very useful means of determining approximate particle size for particles less than 20 nm in diameter. With shorter wavelengths better sensitivity is attained. Absorbance provides a convenient way to observe changes in product quality including variations in particle size and presence of aggregates, larger particles, or debris.

The linear relation between absorbance and silica concentration persists only at silica concentrations less than 5–10%. At higher concentrations sols reach a

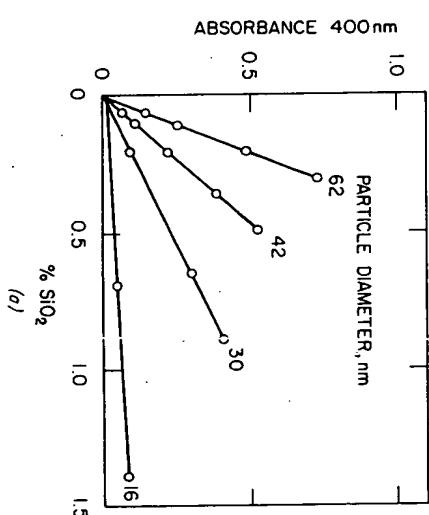


Figure 4.8a. Absorbance of 400 nm light by silica sols of different concentrations and particle sizes.

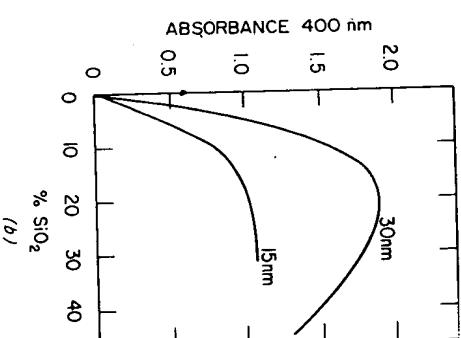


Figure 4.8b. Absorbance of silica sol at 400 nm wavelength showing a maximum is reached in concentrated sols.

maximum turbidity and then become clearer at still higher concentrations, as shown in Figure 4.8b. At first sight it is surprising to observe an almost clear concentrated sol become more turbid as it is diluted. Absorbance is related to light scattering, and scattering is a function of the average distance between silica-water interfaces. As long as particles are separated by several times their diameter, the critical distance is the particle diameter. At a concentration of about 7 vol. % (about 15% by weight) the distance between two particle surfaces is equal to one particle diameter. Hence at higher concentrations the interface-to-interface distance becomes smaller than the diameter, and scattering and absorbance decline. In a very concentrated sol the light, in effect, passes through a mass of silica interrupted by small regions of water which cause the scattering and absorption.

LOW ANGLE X-RAY SCATTERING. Brill, Weyl, and Schmidt demonstrated the use of low angle X-ray scattering for measuring the particle size distribution in relatively dilute sols (158). Samples of colloidal silica of nominal particle size about 15 and 10 nm (Ludox® HS and Ludox® SM) were diluted to about 1% silica. Particle diameters were measured at magnifications up to 32,000 by the electron microscope, with an uncertainty of only about 1 nm. It was concluded that the X-ray and the electron microscope determinations of the distributions of particle diameters in the silica samples agreed within experimental uncertainty. Similar investigation of Ludox® HS is reported by Ja'nni, Kratky, and Sekora (159), who examined solutions as dilute as 0.5% and found a particle diameter of around 18 nm.

By this technique both the particle diameter and the average distances of separation of the randomly spaced particiles can be determined. Using particles ranging from 10 to 50,000 nm in diameter, Dragsdorff (160) showed that for smaller particles a diffraction theory was applicable, whereas with large ones, the geometric optics of a refraction and reflection theory was more useful.

This technique was used to determine particle size of silica sols, which were also determined by electron microscopy and nitrogen adsorption. Lederer (73) reported

that there was almost complete agreement when the particle size distribution was taken into account. However, the conclusion that the particles contained an "inner hydration" of 15-26% by weight of water based on SiO_2 , surely must be in error if the particles were prepared, as stated, by the process by which Ludox® colloidal silica is made (161).

ULTRACENTRIFUGATION. By ultracentrifuging colloidal silica (Ludox®), Hermans and Rijke (162) report that a particle size distribution was observed in agreement with data obtained from electron micrographs by Alexander and Ilter (142). Jennings and Jerrard (155) measured the particle size of Ludox® HS as well as Syton® 2X with an analytical ultracentrifuge, and also by means of the electron microscope and by light scattering, and concluded either sol could be used as a calibration medium:

| Sol | Particle Diameter (nm) | | |
|-----------|------------------------|---------------------|------------------|
| | Ultracentrifuge | Electron Microscope | Light Scattering |
| Ludox® HS | 17.4 | 19.9 | 19.5 |
| Syton® 2X | 14.2 | 14.5 | 14.2 |

Differences in the case of Ludox® were attributed to a wider distribution of particle sizes. The particle size distribution in sols Ludox® HS and SM was examined by Pertoft et al. (145) and some particles were found with extreme sizes of 8-25 and 5-15 nm, respectively.

SEPARATION OF PARTICLES BY SIZE. The classical method of separation is by centrifugation. Very high gravitational force is needed, corresponding to rotor speeds greater than 10,000 rpm for particles smaller than about 30 nm diameter. Various methods requiring less expensive equipment have been investigated. Some progress has been made using chromatographic equipment, which is also expensive but more generally available.

Burns and Chilton (163) patented a method based on gel-permeation chromatography. A dextran gel with 40-120 micron pores was used as column packing. A silica averaging 6 million molecular weight (average 20 nm particles) was separated into a range of molecular weight. Beads of porous glass were used as column packing for exclusion chromatography of colloids by Coll, Fague, and Robillard (164). In the case of silica under the conditions used, the double layer at pH 9.5 was 6 nm thick so that the effective diameter was 12 nm larger than the particle diameter and effective pore diameters in the beads 12 nm smaller than actual size.

Hydrodynamic chromatography, in which sol particles of different sizes are distributed differently along a wall in streamline flow, has been used to separate colloidal particles. Small (165) has described the technique and patented (166) its utility for separating submicron sized particles. However, it probably will not be applicable to very small colloidal particles. In connection with this technique, Stolets, Poehlein, and Vanderhoff (167a) have proposed a mathematical model.

Further developments in sedimentation

Giddings and co-workers (167b, 167c).

A new method of separating latex particles by continuous electrophoresis may become useful for colloidal silica. McCann et al. (168) found that under certain conditions of ionic charge and ionic strength, particles of different sizes migrate at different rates during electrophoresis, and they designed a separation device taking advantage of the phenomenon.

SUBCOLLOIDAL SPECIES. The characteristics of a silica sol can be affected markedly by the presence of relatively small amounts of so-called "active" silicas such as monomer, $\text{Si}(\text{OH})_4$, low polysilicic acids, or in alkaline solutions, silicate ions. These are all detectable by reacting the sol with molybdc acid and noting the rate of formation and amount of the yellow silicomolybdc complex. Some authors arbitrarily define silica that react with molybdc acid within 3-5 min as type A, and that which reacts more slowly as type B. A typical color development curve by Goto and Okura (170) is shown in Figure 4.9, for a sol of small particle size which was diluted about tenfold when added to molybdc acid reagent. In the original sol there would be 100-200 ppm of monomeric silica in solubility equilibrium with the particles. When it is diluted in the acid medium, further dissolution does not instantly occur, so initially about 20 ppm of rapid-reacting silica monomer is found. The colloidal or polymeric fraction (type B) continues to depolymerize at a fixed rate giving a line of constant slope which, according to the authors, gives the initial concentration of monomer present when extrapolated to zero time. The rate of development of color from type B silica, which is the rate of depolymerization, depends on the conditions

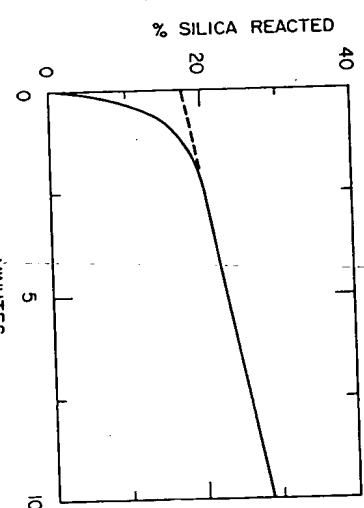


Figure 4.9. Reaction of colloidal silica with molybdc acid. [After Goto and Okura (170).]

under which the polymer or particles have been prepared. In another study, Goto (171) suggests that the depolymerization is accelerated by molybdic acid and is proportional to the total surface area presented by the colloidal silica particles. In similar studies, Baumann (172) stops the development of the yellow color by adding citrate and then determines the silica by converting the yellow complex to molybdenum blue, which gives a more precise measurement of the silica concentration.

Colloidal solutions in which the particles are sufficiently small to be more soluble than massive amorphous silica generally contain 110–150 ppm SiO_2 as monomer, and if stabilized at about pH 9, also HSiO_3^- ions.

The question has been raised whether at equilibrium at pH 9–10, there are polysilicate ions as well as HSiO_3^- and $\text{Si}(\text{OH})_4$, present. Iler finds that in an aged sol, the rate of reaction of silica particles with molybdic acid is not changed by removing the colloid by centrifuging and rediluting with water, indicating that no polysilicates are present.

Specific Surface Area

In sols where the particles are greater than 5 nm in diameter, and are relatively uniform with a normal distribution of sizes about an average value, determination of the specific surface area provides a rapid and dependable method for estimating average size. If, on the other hand, the sols contain particles varying widely in size, such as is often the case with sols made from pyrogenic silicas or other redispersed powders, the results may be misleading.

The relation between particle size determined from electron micrographs and the specific area of the silica as determined by nitrogen adsorption at low temperature (the BET method) was first worked out by Alexander and Iler (66), as previously discussed.

In general, the particle diameter calculated from specific surface area is somewhat smaller than the diameter that would be judged by eye from electron micrographs, because smaller particles may remain unobserved yet contribute substantially to the specific surface. Thus, for example, in an electron micrograph of 100 nm silica particles, 0.1% of 5 nm silica would not appear to be particularly significant, but it would increase the apparent specific surface area of the larger particles from 25 to 30 $\text{m}^2 \text{ g}^{-1}$. Also the particles may have a surface roughness not seen in the electron micrographs.

The usual method of determining specific surface area is to acidify a sol to about the neutral point, add an equal volume of *n*-butyl or *n*-propyl alcohol, and permit the sol to gel and then air-dry. Under these conditions, the silica particles form an open-network gel with minimum points of contact between particles and thus minimum loss of surface area upon drying. The dried powder is then heated to 150°C to drive off physically adsorbed water and alcohol and the surface area determined by one of several adsorption methods.

NITROGEN ADSORPTION. The BET method of nitrogen adsorption (173) is the most dependable and accurate and is further discussed in detail in Chapter 5. Rapid

flow equipment based on principles of gas phase chromatography (174). Applicability of the flow method to silica was studied by Eberly (175), who reported good agreement with the equilibrium isotherm method. Ette and Cieplinski (176) have surveyed the gas chromatographic methods and applications.

ADSORPTION FROM SOLUTION. The adsorption of methyl red dye from an organic solvent has been used as an alternative to nitrogen adsorption, but is more time-consuming (177, 178). The dye is adsorbed only on a silica surface that is fully hydroxylated, that is, has been generated in water and dried at moderate temperature. Adsorption of a fluorescent dye such as Rhodamine B was used by Kautsky and Michel (179). When adsorbed as a cation, the dye fluoresced rose-red, but when not ionized was bluish red. It might be useful for determining surface area of fully hydroxylated silica as present in a sol since it can be adsorbed from water. Unger and Vydra (180) used the adsorption of $\text{Zn}(\text{NH}_3)_6^{2+}$ or $\text{Zn}(\text{en})_3^{2+}$ from aqueous solution on silica powders to determine surface area. Equilibrium is reached after shaking the powder in the solution for 5 hr. The specific surface area is given by the equation

$$A = 480c + 6.6$$

where A is expressed in square meters per gram and c is millimoles $\text{Zn}(\text{en})_3^{2+}$ adsorbed per gram of silica. Solution composition and conditions were as follows: 0.1 M Zn; 2.0 M NH_4NO_3 ; 0.4 M $\text{NH}_4\text{C}_2\text{H}_5\text{NH}_2$; pH = 8.2; 20°C; 1 gram SiO_2 shaken with 25 ml solution for 5 hr and the filtered solution analyzed for decrease in Zn.

A method employing radioactive hafnium could probably be developed, based on the work of Stryker and Matijević (181).

TITRATION METHOD. Adsorption of base on the surface of sol particles provides a rapid estimate of the area of the silica-water interface. The sol rather than a dried powder is used in the Sears (182) method of titrating the silica surface with alkali in strong salt solution between pH 4.0 and 9.0. As discussed in Chapter 3, it provides the simplest way to follow the change in the specific surface area and thus particle size when the silica particle are smaller than 5–10 nm. However, it is equally useful for larger particles, up to a micron or more in diameter, provided it can be shown that the particles are not microporous by comparing results with the area determined by nitrogen or water vapor adsorption, or from electron micrographs.

The method is mainly of value for comparing relative surface areas of particle sizes in a given system which can be standardized. Under these conditions results are reproducible within $\pm 5\%$. Where there are variations in the types of silicas, differences from BET values may range up to $\pm 10\%$.

The sol sample containing 1.50 grams SiO_2 is diluted with CO_2 -free water at 25°C to a concentration of 2–3% SiO_2 , acidified with HCl to about pH 3, and diluted to 135 ml volume. Then 30 g pure crystalline NaCl is added and the mixture stirred rapidly. As soon as the salt is dissolved, the pH is adjusted to pH 4.00 with 0.1 N

The mixture is rapidly titrated to pH 9.00 with 0.1 N NaOH and the volume noted after the pH has remained at 9.00 ± 0.05 for about 1 min. (If the particles are not porous, the end point is stable.)

Although there have been some past variations in the equation relating titration volume to specific surface area, a series of tests by Iller on five well-aged soils ($50\text{-}420 \text{ m}^2 \text{ g}^{-1}$) made originally at high temperature gave average values corresponding to

$$A = 26.4(V_t - V_b)$$

where A is square meters per gram determined by the BET method, V_t the milliliters NaOH required for 1.50 gram SiO_2 , and V_b the titration blank in the absence of silica, usually about 0.3 ml (compare equation in Chapter 3).

It is possible that sol particles may vary in their surface roughness. Also the areas determined by nitrogen adsorption may depend to some extent on the method of drying the sol. The method used above for determining A by nitrogen adsorption involved deionizing the sol with mixed anion-cation exchange resins, adjusting the pH to 2.0, and letting the sample evaporate at $25\text{-}40^\circ\text{C}$ until just gelled; the wet gel was dispersed in at least a tenfold weight of *n*-propanol and air-dried, and samples were then heated in air at 150 and 350°C for 16 hr and the area determined by nitrogen-adsorption by the standard BET procedure. The BET values on duplicate samples dried at the two temperatures varied less than $\pm 2\%$. When particles are smaller than 7-8 nm in diameter, even the most careful techniques of gelling and drying silica may fail to prevent loss of surface area by particle-to-particle contact.

RATE OF DISSOLUTION OF PARTICLES. The relation between particle size and rate of dissolution of silica particles has been reviewed in detail in Chapter 1.

It is logical to assume that the rate of depolymerization or dissolution of colloidal silica particles would be proportional to the specific surface area. Thus different solvents such as dilute hydrofluoric acid, molybodic acid, or dilute alkali, all of which convert the monomeric silica permanently to other silicon compounds, may therefore be employed to measure surface area. The difficulty, however, is that the types of silica particles studied have been so varied and ill-defined that this approach has not been of any value until recently, when sols of uniform discrete solid particles have become available. Even then the value of the method is in doubt unless one can be sure that the samples of silica under study all have the same composition and structure. Variables in the rate of dissolution per unit of surface area include the following:

1. Degree of porosity or internal hydration in the form of uncondensed silanol groups.
2. Amounts of impurities, especially aluminum in the case of particles dissolving in alkali.

3. Particle size, since particles smaller than 5 nm.
4. Nonuniform particles; smaller ones dissolve more rapidly.

Ionic Charge On Particles

The ionization of the silanol groups at the silica-water interface has been dealt with in Chapter 3 in connection with the polymerization of silica. The isoelectric point and point of zero charge of silica are at about pH 2. The rate of condensation of SiOH groups to siloxane bonds ($\text{Si}-\text{O}-\text{Si}$) as well as the rate of the reverse hydrolysis reaction are at a minimum at this pH, because the reactions involve the SiO^- ion:

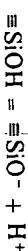


Thus even though silica particles bear little or no charge at pH 2 and can collide, the formation of $\text{Si}-\text{O}-\text{Si}$ bonds between particles and formation of gel is slow.

However, it is only above about pH 7 that a sufficient concentration of negative ionic charges is developed on the surface of the particles to cause mutual repulsion, thus stabilizing the sol against gelling. At intermediate pH's, gelling is most rapid.

Nature of Ionic Charge

As will be further discussed in Chapter 6, the negative charge on the surface of amorphous silica can be represented in a number of ways. One view is that the silica structure is sufficiently open that a hydroxyl ion can occupy a space in the surface, so that the coordination number of each adjacent silicon atom is increased by a fractional amount (see Figure 1.11). Another representation involves ionization of surface silanol groups:



In addition to the studies referred to in connection with the ionization of mono- and polysilicic acids in Chapter 3, many more data are available on sols and gels. Bryant (183) studied the effect of particle size and electrolyte concentration on the pH titration curve of silica sols and interpreted results in terms of the theory of polymeric electrolytes, taking into account the preferential adsorption of cations and also that at high pH the particles dissolve as silicate. In the pH range from 3.5 to 10.5 hydroxyl ions are adsorbed by the silica surface in amounts increasing with pH, as shown by Bolt (184) (see Figure 4.10). The concentration of anionic charges can be expressed as milliequivalents of base per square meter of area, or as the number of hydroxyl ions or charges per square millimeter. Bolt used a commercial silica sol with particles 15 nm in diameter, having a specific surface area of $180 \text{ m}^2 \text{ g}^{-1}$ and found the same values at concentrations from 3 to 30% silica. Heston, Iller, and

(about $8 \text{ H}_2\text{O nm}^{-2}$) the sol is peculiarly unstable and gels. When more water is added the sol becomes more stable.

Similarly sols can be prepared in ether glycols which are polar enough to be miscible with the aqueous sol as water is evaporated, but an organosol forms in a somewhat more volatile solvent. Stable sols containing up to 60% SiO_2 were made with water-miscible alkoxylethanol, $\text{ROC}_2\text{H}_5\text{OH}$ where R is a lower alkyl group (451). However, sols in ethylene glycol monoethyl ether from which water was removed at low temperature under vacuum were claimed not to contain esterified silica (452). If so, then the stability must be due to steric stabilization by hydrogen bonding of the silanol surface with the ether and hydroxyl oxygen atoms. In an earlier patent, this type of sol was heated to stabilize it, which probably effected esterification (453).

A silica powder redispersible to an organosol can be obtained by completely esterifying the surface of colloidal particles before the sol is dried (442). The starting sol must be free from ionic impurities and is first transferred from water to a water-miscible polar organic liquid like *n*-propyl alcohol and then esterified by heating under pressure or transferred to another alcohol and heated to complete the esterification, and dried. The nature of the organic coating determines the colloidal solubility of the powder in a particular organic solvent. A similar process was later claimed by Mindick and Curtis (454) for making an organic-dispersible powder.

Removal of salt from an aqueous sol at low pH can be effected by dilution with a water-miscible organic liquid like dimethylformamide or ethylene carbonate which precipitates the salt. Then the mixture is distilled under vacuum to obtain an anhydrous organosol. In the case of carbonate esters hydrolysis probably provides alcoholic hydroxyl groups for esterification (455). Complete esterification of the surface of the particles is not needed for stability if the dispersion medium is a strong hydrogen-bonding agent. Sol's of which less than half of the surface is esterified with a water-miscible alcohol are stable in an excess of the alcohol (456).

Various methods have been used to dehydrate the esterification reaction mixture and promote reaction. Azeotropic distillation is usually involved. Once the mixture is anhydrous it is often heated under superatmospheric pressure to accelerate the reaction. Water may be removed from the system with a molecular sieve (457). The silica may be in an emulsified mixture of water and immiscible solvent such as mineral oil and cetyl-oleyl glycol ether and an emulsifying agent. This is dehydrated in a climbing-film evaporator (458). Water can be removed by reaction with a ketal according to Ryznar (459).

Silylation

A still more stable organophilic surface on silica particles is obtained by reacting the surface with alkyl chlorosilanes, thus attaching organosilyl groups. For example, the surface of colloidal silica was covered with trimethylsilyl groups by Iler (460), who transferred silica from water to triethyl phosphate, dried the sol, added trimethylchlorosilane, then heated and removed excess reagent and solvent by vacuum evaporation. The solid product was dispersible to form sols in benzene, ether, and chloroform, but not in water.

Dispersions of silica particles completely hydrophobed with methylsilyl groups covering the surface have been studied in propanol-water media by Benitez, Contreras, and Goldfarb (461). It was observed that the particles have surface and interfacial tensions similar to those of paraffin wax. Wetting of the powder occurred in alcohol-water mixtures containing more than 15% propanol, 32% ethanol, and 50% methanol. The dispersion process does not appear to involve electrostatic repulsion but rather the interfacial free energy which is closely related to wetting behavior.

Silica particles in a sol can be rendered organophilic by reaction in a water-*t*-butyl alcohol medium with mono or dimethylchlorosilanes according to Iler (462). The surface-modified particles are transferred to an organic phase and dehydrated by distillation.

Silica hydrosol of 3-5 nm particles emulsified with mineral oil was water-stripped and reacted with polydimethylsiloxane oil to obtain a hydrophobic antifoam agent (463).

COMMERCIAL COLLOIDAL SILICAS

Because of the constantly changing developments and demands, new types of commercial silica sols become available and others disappear from the market. It is not possible therefore, to predict which kinds will remain available in the future, but past and current types are listed in Table 4.3, which includes some products that are no longer available but may have been referred to in earlier technical publications. Most of the sols contain particles 5-50 nm in diameter and with 30-50% by weight of silica. Most are stabilized by alkali, either sodium hydroxide or ammonium, with pH between 8 and 10; a few are stabilized at low pH by special purification, by replacing the water by a polar organic solvent or by giving the particles a positive charge with alumina. Commercial sols consist of discrete particles with very little aggregation, since at high concentration any appreciable degree of aggregation would greatly increase viscosity.

Dispersions can be made from certain grades of pyrogenic silica powders; these are considered in Chapter 5. In powders with bulk densities less than about 5 lb ft^{-3} the individual particles are so weakly linked that they can be dispersed at least to aggregates of colloidal size in water at pH 9, by strong mechanical agitation or shearing action. Powders of lowest bulk density and lowest specific surface area or largest primary particle size can be dispersed most completely to sols. Since in many references to applications it is not possible to distinguish between the sources of the sols, the uses of sols of all types are considered in the following section.

USES OF COLLOIDAL SILICAS

In the following survey it is not possible to indicate the relative practical value or importance of specific uses. It will mainly serve as a guide to the literature for those engaged in application research. Only a small fraction of the issued patents related

Table 4.3. Properties of Commercial Silica Sols Listed by Manufacturer

| Sol (Manufacturer) | Grade | SiO ₂ (%) | Stabilizer | | Ratio SiO ₂ :Na ₂ O | pH | Particle Diameter (nm) | Specific Surface (m ² g ⁻¹) | Technical Bulletin |
|----------------------------------------------------------------|--------------------|-------------------------|--------------------------------|-------------------|----------------------------------------------|------|------------------------------|----------------------------------------------------------|-----------------------|
| | | | Type | (%) | | | | | |
| Ludox® (E. I. du Pont de Nemours & Co., Wilmington, Del.) | HS-40 | 40 | Na ₂ O | 0.41 | 95 | 9.7 | 12 | 230 | E10260 (1976) |
| | HS-30 | 30 | Na ₂ O | 0.32 | 95 | 9.8 | 12 | 230 | E10260 (1976) |
| | TM | 50 | Na ₂ O | 0.21 | 240 | 9.0 | 21 | 130 | E10260 (1976) |
| | SM | 30 | Na ₂ O | 0.56 | 54 | 9.9 | 7 | 360 | E10260 (1976) |
| | AS ^a | 40 | NH ₃ | — | — | 9.0 | 21 | 130 | E10260 (1976) |
| | LS | 30 | Na ₂ O | 0.10 | 300 | 8.2 | 12 | 130 | E10260 (1976) |
| | WP ^b | 35 | Na ₂ O | 0.62 | 130 | 11.0 | 21 | 130 | E08913 (1976) |
| | (AS) ^c | 30 | NH ₃ | — | — | 9.6 | 13-14 | 210-230 | A82273 (1974) |
| | AM ^d | 30 | Na ₂ O | 0.13 | 230 | 9.0 | 15 | 210 | A21163 |
| Positively charged sols—Al ₂ O ₃ coating | | | | | | | | | |
| Nalcoag® (Nalco Chemical Co., Chicago, Ill.) | 130M ^e | 30 | C1 | 0.9 | — | 4.4 | 13-15 | 210 | A83845 (1973) |
| | CL-X | 46 | — | — | — | 9.1 | — | — | ED9550 (1976) |
| | 1115 | 15 | Na ₂ O | 0.8 | 19 | 10.4 | 4 | 750 | K-1115 |
| | (2326') | 14.5 | Na ₂ O | 0.01 | — | 9.0 | 5 | 600 | K-2326 (1975) |
| | (E136 | 1130 | 30 | Na ₂ O | 0.65 | 46 | 10.0 | 8 | K-1030 (1976) |
| | 1030 | 30 | Na ₂ O | 0.40 | 75 | 10.2 | 11-13 | 375 | 190-270 |
| | 1140 | 40 | Na ₂ O | 0.40 | 100 | 9.7 | 15 | 200 | K-1140 (1972) |
| | 1050 | 50 | Na ₂ O | 0.35 | 143 | 9.0 | 17-25 | 120-176 | K-1050 (1976) |
| | 1034A ^f | 34 | — | — | — | 3.1 | 16-20 | 135-190 | K-1034 (1972) |
| | (1129 ^g | 30 | — | — | — | 3.5 | 16-25 | 150 | Data sheet (1974) |
| | (E-127 | 35 | — | — | — | 5 | 20 | 150 | K-2325 (1975) |
| | (2325 ^h | 40 | NH ₃ | 0.10 | — | 9.3 | 20 | 150 | K-2327 (1975) |
| | (41D01 | — | — | — | — | — | — | — | — |
| Nyacol® (Nyacol, Inc. Ashland, Mass.) | 2600 ⁱ | 57 | Na ₂ O | 0.10 | — | — | 20 | 150 | Data sheet (1973) |
| | 1060 | 50 | Na ₂ O | 0.25 | — | 8.5 | 60 | 50 | K-1060 (1975) |
| | 40D04 ^j | 50 | — | — | — | 4.0 | 16-22 | — | — |
| | D2149 ^m | 30 | NH ₃ | 0.03 | — | 9.5 | 12-15 | 210 | — |
| | D2361 ⁿ | 30 | Al ₂ O ₃ | 1.8 | — | 3.8 | 20 | 150 | — |
| | 215 | 15 | Na ₂ O | 0.75 | — | 11 | 3-4 | — | — |
| | 830 | 30 | Na ₂ O | 0.45 | — | 10.7 | 8 | — | — |
| | 1430 | 30 | Na ₂ O | 0.35 | — | 10.4 | 14 | — | — |
| | 40 | Na ₂ O | 0.48 | — | — | 10.4 | 14 | — | — |

^a Data supplied
(1976)

| | | | | | | | | |
|--------------------------------------------------------------------------------------------|-----|--------------------------------|-----------|------|----------|-------|---------|---------------------------------|
| 1130 | 30 | Na ₂ O | 0.65 | 46 | 10.0 | 8 | 375 | K-1030 (1976) |
| 1030 | 30 | Na ₂ O | 0.40 | 75 | 10.2 | 11-13 | 190-270 | |
| 1140 | 40 | Na ₂ O | 0.40 | 100 | 9.7 | 15 | 200 | K-1140 (1972) |
| 1050 | 50 | Na ₂ O | 0.35 | 143 | 9.0 | 17-25 | 120-176 | K-1050 (1976) |
| 1034A ^a | 34 | | | | 3.1 | 16-20 | 135-190 | K-1034 (1972) |
| (1129 ^b | 30 | | | | 3.1 | 16-25 | 150 | Data sheet (1974) |
| E-127 | | | | | | | | |
| (2325 ^c | 35 | | | | 5 | 20 | 150 | K-2325 (1975) |
| (43125 | | | | | | | | |
| (2327 ^d | 40 | NH ₃ | 0.10 | — | 9.3 | 20 | 150 | K-2327 (1975) |
| (41D01 | | | | | | | | |
| 2600 ^e | 57 | Na ₂ O | 0.10 | — | — | 20 | 150 | Data sheet (1973) |
| 1060 | 50 | Na ₂ O | 0.25 | — | 8.5 | 60 | 50 | K-1060 (1975) |
| 40D04 ^f | 50 | — | — | — | 4.0 | 16-22 | — | |
| D2149 ^m | 30 | NH ₃ | 0.03 | — | 9.5 | 12-15 | 210 | |
| D2361 ⁿ | 30 | Al ₂ O ₃ | 1.8 | — | 3.8 | 20 | 150 | |
| Nyacol® (Nyacol, Inc. Ashland, Mass.) | | | | | | | | |
| 215 | 15 | Na ₂ O | 0.75 | 11 | 3-4 | — | | |
| 830 | 30 | Na ₂ O | 0.45 | 10.7 | 8 | — | | |
| 1430 | 30 | Na ₂ O | 0.35 | 10.4 | 14 | — | | |
| 1440 | 40 | Na ₂ O | 0.48 | 10.4 | 14 | — | | |
| 2050 | 50 | Na ₂ O | 0.48 | 10 | 20 | — | | |
| 2034A° | 34 | — | — | 3.5 | 20 | — | | |
| 2046EC | 46 | Not given | 9.8 | 20 | — | — | | |
| 1430 NH ₃ | 30 | NH ₃ | 0.2 | 9.4 | 13-15 | — | | |
| Snowtex® (Nissan Chem. Industries, Ltd., Tokyo, Japan; 200 Park Ave. New York) | 20 | Na ₂ O | 0.35 | — | 9.5-10 | 10-20 | — | |
| C | 30 | Na ₂ O | 0.6 | — | 9.5-10.5 | 10-20 | — | |
| N ^p | 20 | Na ₂ O | 0.2 | — | 8.5-9.0 | 10-20 | — | |
| O ^p | 20 | Na ₂ O | 0.04 | — | 9.0-10.0 | 10-20 | — | |
| | | | | 3-4 | 10-20 | — | | |
| Syton® (Monsanto, Ltd. London, England) | W15 | 15 | Not given | — | 9.8-10.6 | 36 | 75 | No. 53-3 (E) M-E-2 (1975) |
| | W30 | 30 | Not given | — | 9.8-10.6 | 36 | 75 | |
| | W50 | 50 | Not given | — | 9.8-10.6 | 36 | 75 | |
| | T15 | 15 | Not given | — | 9.6-10.2 | 18 | 150 | |
| | T30 | 30 | Not given | — | 9.6-10.2 | 18 | 150 | |
| | X30 | 30 | Not given | — | 9.6-10.2 | 11 | 250 | |
| | D30 | 30 | Not given | — | 9.5-10.0 | 8.5 | 325 | |

ious systems, silicates and alkoxides, and can serve as a basis for understanding silica th of monodisperse sols.

mercial methods of preparation that use s continuous phase. The Ramsay et al. at the method of preparation has on the ion of silica particles prepared by methods

Vrij chapter is an excellent overview of the n aqueous systems. This overview includes s. Further information regarding this area his book entitled "Sol-Gel Technology". chapter presents findings from hydrolysis t systems. Here reverse micelles are used ethylorthosilicate.

demonstrates how nucleation and polymer- f silica gels and subsequently silica-based Healy's chapter, which presents a model of n effected by pH changes and addition of references (1-14) is included.

36; 1865, 135, 65.
of *Silica and Silicates*; Cornell University Press:

Wiley: New York, 1979.

ia, I. *Chem. Express* 1987, 2(6), 333-336.

Marcandalli, B.; Bellobono, I. R.; Ridoglio, G.
437-455.

in 1985, 2, 10-15.

js. 1987, 87(10), 5634-5643.

Gel Science: The Physics and Chemistry of Sol-
oston, MA, 1990.

), 265-275.

Sci. Ceram. 1988, 14, 125-131.

5(6), 22-28.

id Interface Sci. 1988, 124(1), 140-210.

Dzhumagaziev, M. T.; Kompleksn. Ispol's. Miner.
(), 265-275.

, E. *Colloids Surf.* 1987, 27(1-3), 121-131.

Silica Nucleation, Polymerization, and Growth Preparation of Monodispersed Sols

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The industrial development of silica sol manufacturing methods is reviewed. Primary attention is focused on the preparation of mono- dispersed sols from water glass by the ion-exchange method. Details are given for variations of manufacturing process and for the characteristics of both the processes and sols obtained. Furthermore, the following surface modifications of particles are demonstrated: silica sols stabilized with ammonia, amine, and quaternary ammonium hydroxide; aluminum-modified or cation-coated silica sol; and lithium silicate. Finally, future trends in silica sol manufacturing are discussed from the viewpoint of not only raw materials and improvement of the procedures but also the function of the silica sols and their particle shape.

MONODISPERSED SOL IS COMMONLY REFERRED TO as silica sol or colloidal silica. The term "colloidal silica" here refers to a stable dispersion of discrete, amorphous silica particles.

The industrial development of silica sols first began with the initial research by Graham (1) in 1861 involving the addition of hydrochloric acid to an aqueous solution of sodium silicate followed by dialysis to obtain dilute silica sol. In 1933, silica sol containing 10% SiO₂ was first marketed. This step was followed in 1941 by the announcement of an ion-exchange process (2), including procedures for stabilization and for concentration of the sol by heating, that used an ion-exchange resin to remove sodium ions

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from the dilute aqueous solution of sodium silicate. This sodium removal process is the most common today. In 1951, a process (3) for creating colloidal silica particles of uniform and controlled size was announced for the first time. In 1956, a method (4) was established for making stable sols consisting of microscopic particles having a diameter of only 8 nm yet containing more than 30% of silica. The history of the development of silica sols and a description of the fundamental and application research up to and throughout the 1950s was summarized in detail by Iler (5). Various raw materials can be used in the manufacturing of monodispersed sol. Examples of these materials include silicon metals (6), silicon tetrachloride (7), ethyl silicate (8), water glass (2), and silica powder (9). In this chapter, I focus attention on the preparation of monodispersed sols from water glass, a raw material that is presently used in large amounts industrially for the inexpensive production of silica sols.

The manufacturing processes of silica sols can be broadly divided into the following three steps:

1. formation of active silicic acid by removal of alkali ions from a dilute aqueous solution of water glass
2. formation of a dilute silica sol by nucleation from the active silicic acid and growth of discrete silica particles by polymerization
3. concentration of the dilute silica sol

In addition, I will discuss modification of the surfaces of silica particles.

Manufacturing Methods of Silica Sols and Their Characteristics

History of Silica Sol Manufacturing Methods. Although numerous techniques have been proposed for manufacturing silica sols, including dialysis (10), electrodialysis (11), peptization (12), acid neutralization (13), and ion exchange (3, 14), the last three methods have come to be used most commonly. At present, the ion-exchange method is considered the most prominent technique.

Although the dialysis method, which involves the reaction of dilute water glass with an acid followed by dialytic removal of the sodium salt as the formed electrolyte, was proposed in 1861, it was never applied on an industrial basis. Furthermore, the electrodialysis method was attempted in various ways as a method for electrically removing sodium salt from water glass. But, unlike the last three methods mentioned, it did not reach the level of practical application.

Peptization Method. As shown in Figure 1, an acid such as sulfuric or hydrochloric is added to a dilute aqueous solution of water glass while stirring, or while heating as necessary, to neutralize and obtain a silica gel containing salt. Next, the crude silica gel is washed with water to remove the salt and obtain a silica wet gel. Then, water and an aqueous sodium hydroxide solution are added to the gel so that the pH of the resulting solution is 8.5–10 and a silica gel slurry is formed. The slurry is then heated for several hours in an autoclave at 120–150 °C to allow the gel to peptize and form a sol. Thus, a silica sol is prepared. For example, the resulting silica sol contains 30 wt% SiO₂, has a pH of 10, has a molar ratio of SiO₂:Na₂O of about 100, and consists of irregular particles having a diameter of 10–20 nm. However, it is difficult to obtain silica sols having a desired particle size or high purity with this method.

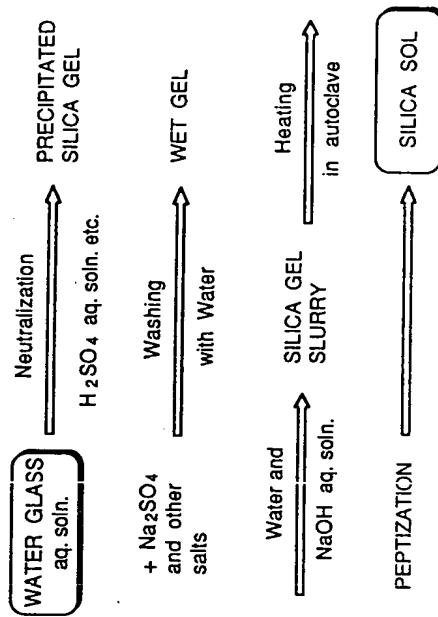


Figure 1. Flow chart of peptization method for manufacturing silica sols.

Acid-Neutralization Method. As is indicated in Figure 2, an acid, such as sulfuric or hydrochloric, is added to a dilute aqueous solution of water glass while heating and stirring. This addition results in silica sol nucleation and particle growth to obtain a dilute silica sol containing salt. The salt is removed by either dialysis or electrodialysis, and the solution is concentrated to obtain a silica sol. In recent years, as the removal of salt has been made easier through the use of ultrafiltration membranes, this method has come to be considered as having potential for the future.

Ion-Exchange Method. Sophisticated ion-exchange resins have been developed to efficiently remove sodium ions at the industrial application level. This method is currently the primary means of manufacturing silica sols. The following section provides a detailed description of this method.

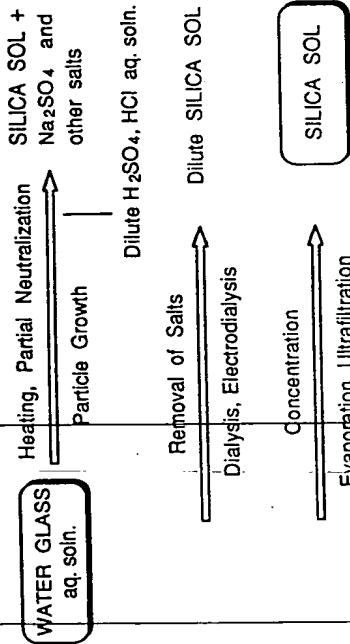


Figure 2. Flow chart of acid-neutralization method for manufacturing silica sols.

Silica Sol Manufacturing Using the Ion-Exchange Method.

The silica sol manufacturing method using ion-exchange is as shown in the basic flow chart of Figure 3.

Ion Exchange. An aqueous water-glass solution as the raw material in this process can have a SiO₂ content of 30%, a Na₂O content of 10%, a molar ratio of SiO₂:Na₂O of 3.1, a specific gravity of 1.2, and a pH of 12–13. Water is added to this aqueous water-glass solution while stirring to obtain a dilute aqueous water-glass solution containing 2–6% SiO₂. In this state the silica takes the form of polysilicate anion. Next, this dilute aqueous water-glass solution is passed through a bed of cation-exchange resin in a column for which hydrogen ions have been regenerated in advance to allow the sodium ions to be adsorbed onto the resin bed and leave an aqueous solution of active silicic acid. This liquid is a microscopic colloidal solution with a pH of 2–4 containing 2–6% SiO₂ comprising particles with a diameter of 2 nm or less. The colloidal solution is also in an unstable state and easily gels upon standing because the degree of polymerization is several hundreds.

Particle Growth. Nucleation (3), polymerization (15), and particle growth (16, 17) are performed on this active silicic acid in the presence of alkali at a temperature of at least 60 °C, a pH of 8–10.5, and a molar ratio of SiO₂:Na₂O of about 20–500, and thus a dilute silica sol is formed. The process of particle growth is discussed in more detail in the next section. The formed dilute silica sol generally consists of spherical particles having a diameter of 4–100 nm, a pH of 8–10.5 and a SiO₂ content of 2–6%. This silica sol is a colloidal liquid in a stable state, and therefore it causes no gelling. As illustrated in the flow sheet, the dilute aqueous water-glass solution is in the form of polysilicate anion. In contrast to this ionic state,

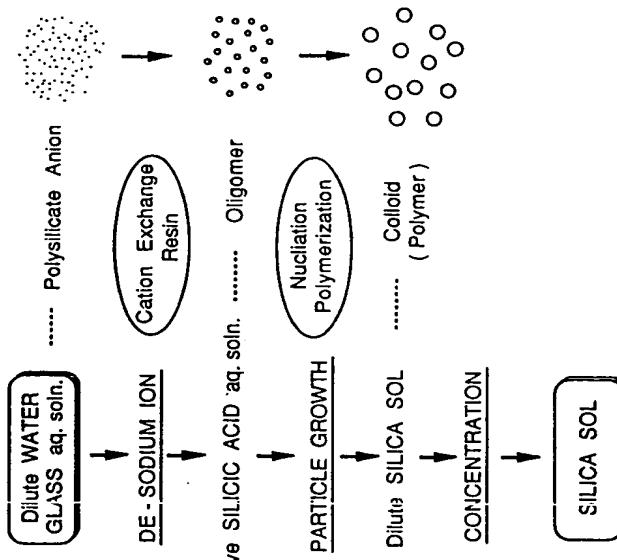


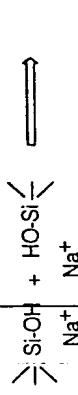
Figure 3. Flow chart of ion-exchange method for manufacturing silica sols.

The active silicic acid is in the form of an oligomer, that is, a colloid of microscopic particles. The dilute silica sol is a polymer in the colloidal state.

Concentration. Next, this dilute silica sol is concentrated so that the SiO₂ content is increased to 15–60%. The concentration is needed not only to ensure efficient transport of a small volume of sol but also for use in silica sol applications, for example, as a binder, a catalyst carrier, and a gelation agent. Because the concentration process of the dilute silica sol efficiently removes the dispersion medium of water, the most common way (3, 14) of accomplishing this step was by using steam under reduced pressure or normal pressure. However, more recently, use of the ultrafiltration membrane (18–20), originally intended for the separation of colloidal size particles, has been evaluated for ion removal; this approach is energy saving. It is actually employed in some applications.

Finished products are obtained after the concentration, pH, and conductivity of the concentrated sol are adjusted to maintain their stability. In actuality, several types of manufacturing methods are used, depending on the particular combination of particle growth and concentration.

Mechanism of Particle Growth. As shown in Scheme I, the silicic acid undergoes dehydrating condensation polymerization in the presence of alkali. The higher the temperature and the pH and the longer the reaction time, the faster the polymerization proceeds. As a result of polymerization, Na^+OH^- that was adsorbed onto the active silicic acid is released and increases the pH.



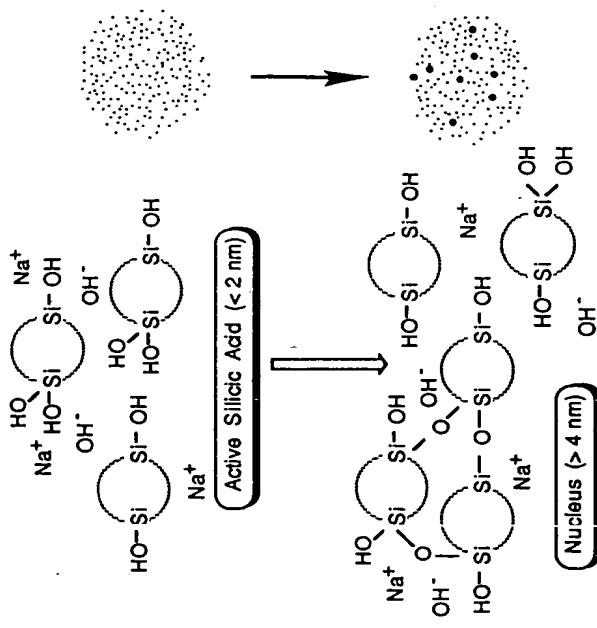
Scheme I. Polymerization of silicic acid by dehydrating condensation.

As shown in Schemes II and III, active silicic acid is polymerized by heating in the presence of alkali and first forms nuclei. Active silicic acid then polymerizes around the nuclei, and thus particles are formed. This process is often referred to as "buildup". In actuality, nucleation and particle growth take place simultaneously. When the temperature is high (such as in autoclave heating), or when the concentration of silicic acid is high during particle growth, particles grow through bonding between nuclear particles or between larger particles, respectively. During nucleation and particle growth as well, Na^+ and OH^- ions are released, and thus the pH of the reaction system is increased. The higher the pH is, the faster the particles grow. However, dissolution occurs if the pH is too high, so pH control is considered to be the most important factor.

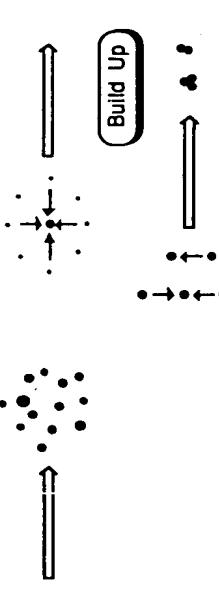
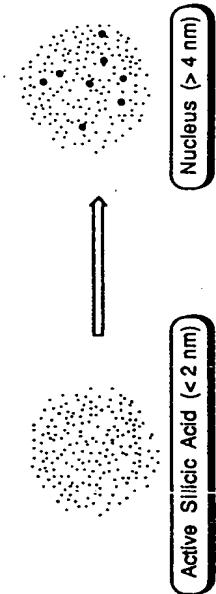
In addition, when the pH of this liquid exceeds 10.5, the formed particles undergo dissolution and hydrolysis and then precipitate, and such dissolution and precipitation take part in the particle growth. The main factors that dominate particle growth are amount of alkali such as Na_2O , silica concentration, $\text{SiO}_2:\text{Na}_2\text{O}$ molar ratio, temperature, time, and method of addition.

Variations of Silica Sol Manufacturing Process. As shown in Figure 4, the four methods, A-1, A-2, B-1, and B-2, use different technical combinations of nucleation, particle growth, and concentration. In any of these methods the raw material aqueous water-glass solution is diluted, and sodium is removed with a cation-exchange resin to obtain an active silicic acid. The characteristics of these four processes are shown in Table I.

Methods A-1 and A-2. In Methods A-1 and A-2, a small amount of an aqueous NaOH solution is added, while stirring, to the acidic active silicic



Scheme I. Polymerization of active silicic acid to form nuclei.



Scheme II. Polymerization of active silicic acid around nuclei to form particles.

acid having a $\text{SiO}_2:\text{Na}_2\text{O}$ molar ratio of 500–1000 until the $\text{SiO}_2:\text{Na}_2\text{O}$ molar ratio is, for example, 80–100 and the solution is stable.

In Method A-1, a fixed amount of this liquid is first charged in an evaporator that is heated from the outside with steam. Simultaneous to the beginning of solution concentration under reduced or normal pressure,

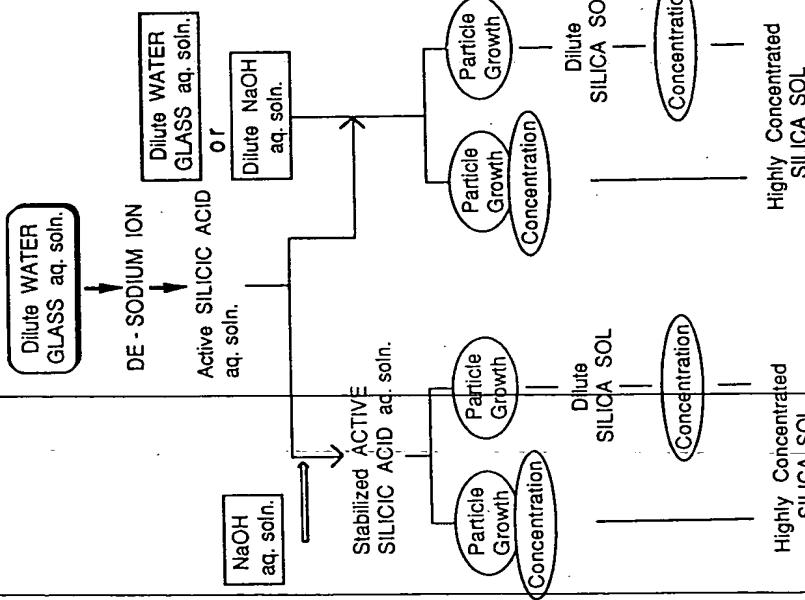


Figure 4. Four methods of silica sol manufacturing.

aqueous active silicic acid solution is continuously metered into the evaporator to carry out particle growth and concentration at the same time.

On the other hand, in Method A-2, particle growth and concentration are carried out separately. In the particle-growth step, a fixed amount of the stable aqueous active silicic acid solution is charged into a heating-aging tank and heated. Continuous charging of the aqueous silicic acid solution then follows to carry out buildup of particles. Alternatively, in another method the stable aqueous active silicic acid solution that was initially charged in the heating-aging tank is simply heated to carry out particle growth. A temperature of 60–150 °C is commonly used for the aging under heating. The dilute silica sol prepared in this manner has a SiO₂ content of 2–6%, a pH of 9–10.5, and a particle size of 4–20 nm.

Next, this sol is passed on to the concentration step. Because the silica

Table I. Characteristics of Silica Sol Manufacturing Methods

| Characteristics | Method A-1 | Method A-2 | Method B-1 | Method B-2 |
|---------------------------------------|---------------------------------------|--------------------------------------------------------------------------------------|----------------------------------------------------|--------------------------------------------------------------------------------------|
| Intermediate material | dilute silica sol | dilute silica sol | silicic acid and water glass separate | silicic acid and water glass separate |
| Particle growth and concentration | simultaneous | separate | simultaneous | simultaneous |
| Change in pH during particle growth | 7 → 9–10.5 | slow | fast | 11.5 → 9–10.5 |
| Particle growth rate | small | initial: hydrolysis of water glass; intermediate to final polymerization of particle | small-large | initial: hydrolysis of water glass; intermediate to final polymerization of particle |
| Size of nuclei | large | possible | possible | large |
| Nucleation mechanism | polymerization of particles | difficult (normal pressure) possible (with pressurization) | possible | easy |
| Manufacturing of large-particle sols | more difficult than in Process B | possible for microscopic- to large-sized particles | possible for microscopic- to large-sized particles | more difficult than in |
| Ease of buildup | Control of particle size | possible | impossible or difficult | possible |
| Control of particle size distribution | Control of particle size distribution | possible | impossible or difficult | possible |
| Manufacturing time | long (longer than in B-1) | short (longer than in B-2) | long | short |

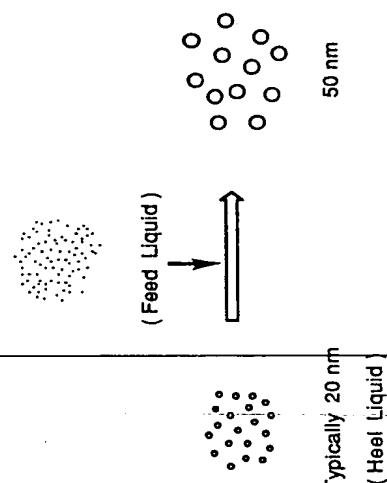
particles have already grown and are in a stable state, concentration can be performed in an arbitrary manner, for example, through evaporation or using an ultrafiltration membrane. The pH, concentration, and conductivity of the highly concentrated sol are then adjusted to obtain a finished sol product.

Methods B-1 and B-2. Characteristically in Methods B-1 and B-2, the aqueous solution of active silicic acid is continuously charged into either a dilute aqueous water-glass solution or dilute aqueous NaOH solution that has preliminarily been heated, and stirred if necessary, to effect particle growth. In Method B-1, concentration and particle growth are carried out simultaneously under conditions similar to those of Method A-1. In Method B-2, particle growth and concentration are carried out separately, and in this regard it is essentially the same as Method A-2. However, in Method B-1 or B-2, larger diameter silica sol particles, 4–100 nm, can be formed. On the other hand, Methods A-1 or A-2 allows production only up to medium-sized silica particles having a diameter of 4–20 nm.

Manufacturing of Large-Particle Silica Sols. A method for manufacturing silica sols consisting of large-diameter particles of 50–200

nm is as follows. The buildup method is used because the growth of particles is difficult in Method A-1 or A-2 even when medium-diameter silica sols are manufactured.

As indicated in Scheme IV, stable dilute sol is nucleated to obtain sols having a particle size of, for example, 20 nm, which is used as a seed. Then, in the next step, an active silicic acid or stable dilute sol is continuously charged onto the seed to allow the silica particles to grow to a diameter of 50 nm. Thus, the process consists of two separate steps. In either Method B nucleation is carried out in the initial stage of the process, and buildup occurs from the intermediate to the final stages. However, this method is not clearly separated into two steps.



Scheme IV. Preparation of silica particles from stable dilute sol using the buildup method.

< Process A >

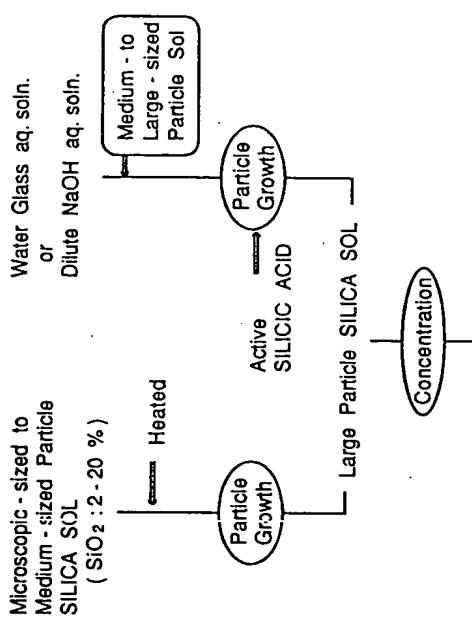


Figure 5. Flow chart of production of large-particle silica sols.

Characteristics of Silica Sols Produced by the Four Methods.
The characteristics of the sols manufactured according to Methods A and B are shown in Table II.

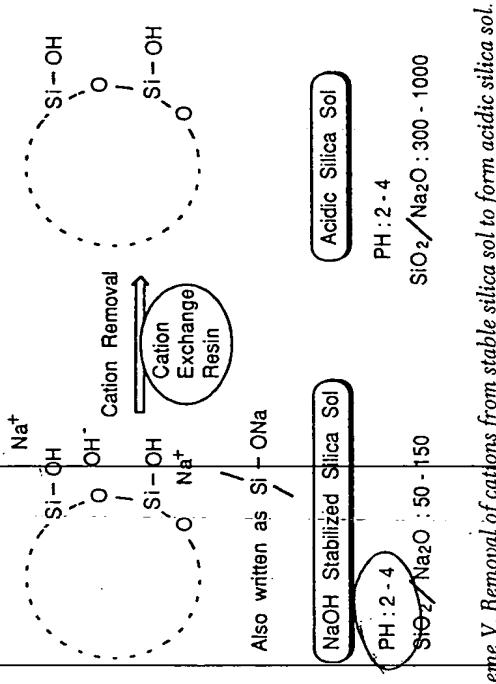
Table II. Characteristics of Sols Formed by the Different Methods

| Characteristics | Method A-1 | Method A-2 | Method B-1 | Method B-2 |
|----------------------------------------|------------|------------|------------|------------|
| Particle size distribution | broad | narrow | broad | narrow |
| Particle shape | irregular | spherical | spherical | spherical |
| Degree of silica particle distribution | low | high | high | high |
| Illustrations of particle shape | ○○○○ | ○○○○ | ○○○○ | ○○○○ |

Figure 5 illustrates the production of large-particle silica sols. In Process A, silica sol consisting of microscopic- to medium-sized particles is heated in an autoclave at 120–130 °C for several hours, and the hydrothermal treated silica sol is concentrated to obtain a highly concentrated large-particle sol. In Process B, medium- to large-particle-size sols, which serve as nuclei, are added to an aqueous water-glass solution or a dilute aqueous NaOH solution. The mixture is then heated to carry out aging while stirring, and in this state active silicic acid is charged to allow buildup of particles. Factors that dominate particle growth are the size and concentration of the silica particles that serve as the nuclei, the amount of active silicic acid to be added, the aging temperature, aging time, pH behavior, and others. Method B characteristically facilitates formation of sols with large particle sizes showing a uniform particle size distribution ranging up to about 200 nm.

Manufacturing Methods of Surface-Modified Silica Sols

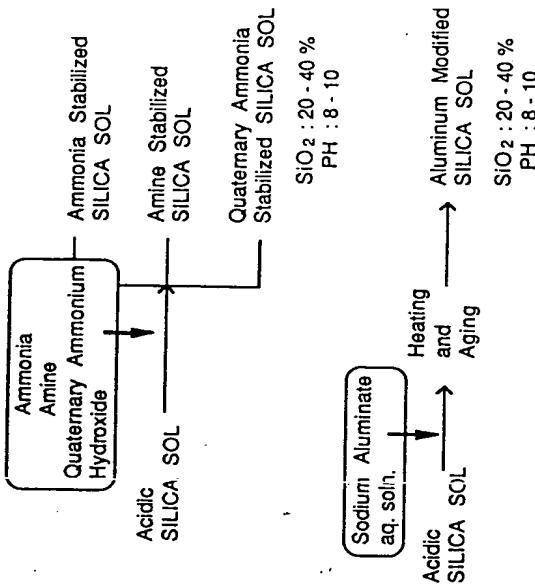
The silica sols described in the manufacturing methods are all generally stabilized with NaOH, and the majority of the silanol groups on the surface of the silica sol are covered with Na⁺ ions, as indicated in Scheme V. Na⁺ ions are strongly adsorbed onto the silanol group, and this condition sometimes is expressed as Si-ONa.



For manufacturing a surface-modified silica sol, an acidic silica sol (20) from which these Na^+ ions have been removed is used in most cases. As shown in Scheme V, silica particles are brought into contact with a cation-exchange resin, and if necessary, with an anion-exchange resin, to obtain an acidic silica sols of pH 2–4. This acidic sol is stable because it is negatively charged even at pH 2–4, according to zeta-potential measurements. Starting from such acidic silica sol, surface-modified silica sols are manufactured.

TDS

Silica Sols Stabilized with Ammonia, Amine, and Quaternary Ammonium Hydroxide. As shown in Figure 6, ammonia (21), amine (22), or quaternary ammonium hydroxide (22) is added to the acidic silica sol while stirring, and if necessary the mixture is aged with heating to obtain a correspondingly stabilized silica sol. Such sols have a SiO_2 content of 20–50% and a pH of 8–12. This type of sol fits new applications because the sols remain mixed for a fixed period with strongly alkaline water glass, CaO , and MgO , with which ordinary silica sols can hardly be mixed because of gelling.



sols cannot be used in this neutral region because they undergo gelation but the aluminum-modified sol has enabled various new applications. The aluminum-modified silica sol is the first surface-modified silica sol that has considerable industrial value.

Cation-Coated Silica Sol. As shown in Figure 7, an aqueous solution of basic aluminum chloride is added to an acidic or alkaline silica sol while stirring, and then a dilute aqueous NaOH solution is added until the pH of the mixture is 4–6. The mixture is then aged by heating to 80–100 °C to form a cation-coated silica sol (24). This silica sol is used in applications where the pH is in the acidic region and where it is used as a mixture with a cationic aqueous solution. Moreover, the cation-coated silica sol can be mixed easily with water-soluble organic solvents. Besides aluminum salt, other basic salts such as of Zr and Ti and cationic surface-active agents (25) can also be used for cation coating.

Lithium Silicate. In this chapter, the term lithium silicate means very small silica sol particles whose surfaces are coated with lithium hydroxide. As shown in Figure 8, this lithium silicate (26) can be prepared by adding an aqueous solution of lithium hydroxide to the acidic silica sol while stirring, and then heating the mixture to a temperature of 60 °C or less for an extended period of time, for example, a half day to several days. This lithium silicate typically has a SiO_2 content of 10–25%, a $\text{SiO}_2:\text{Li}_2\text{O}$ molar ratio of 3–9, and a pH of about 11. Lithium silicate is a kind of water

Figure 9, this new silica sol is elongated. For example, the particles have a diameter of about 10 nm and a length of 50–100 nm. To prepare such elongated silica sols, a calcium salt and an aqueous sodium hydroxide solution are added to an active silicic acid or an acidic silica sol, and the mixture is heated in an autoclave at 100–150 °C for several hours. Thus, particle polymerization takes place in nonuniform directions, and an elongated silica sol (31) can be formed.

Figure 7. Flow chart of production of cation-coated silica sol.

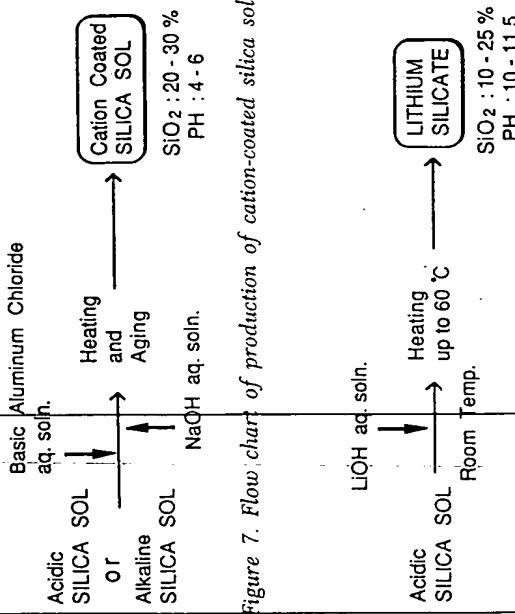


Figure 8. Flow chart of production of lithium silicate.

glass like sodium silicate and potassium silicate, but it is used as a binder because it has particularly high levels of water resistance and heat resistance.

Future Trend in Silica Sol Manufacturing

Silica sols will be required to have more unique and sophisticated characteristics in the future to meet the needs of various application fields (2). Therefore, raw materials will no longer be limited to the aqueous water-glass solutions, but a variety of raw materials will be used corresponding to the specific properties required for the desired silica sol. For example, large- to very large-sized silica sols that are of high purity and as truly spherical as possible are required in electronics applications. Ethyl silicate will most likely be used as a raw material for this purpose. In addition, organosilica sols dispersed in organic solvents, such as methanol silica sol (28) and dioctyl phthalate sol (29), are beginning to be used in the field of plastics modification.

Furthermore, in an effort to discover unknown characteristics of silica sols, further progress will occur in the development of elongated silica sols having shapes other than spherical, such as elongated, fibrous, and platelet. We are currently working on the development of elongated silica sols. Compared with the spherical silica sols, the elongated silica sols have high film-forming properties and demonstrate unique properties as a binder or coating agent for the formation or surface treatment of inorganic fibers. As shown in the transmission electron microscope photographs of

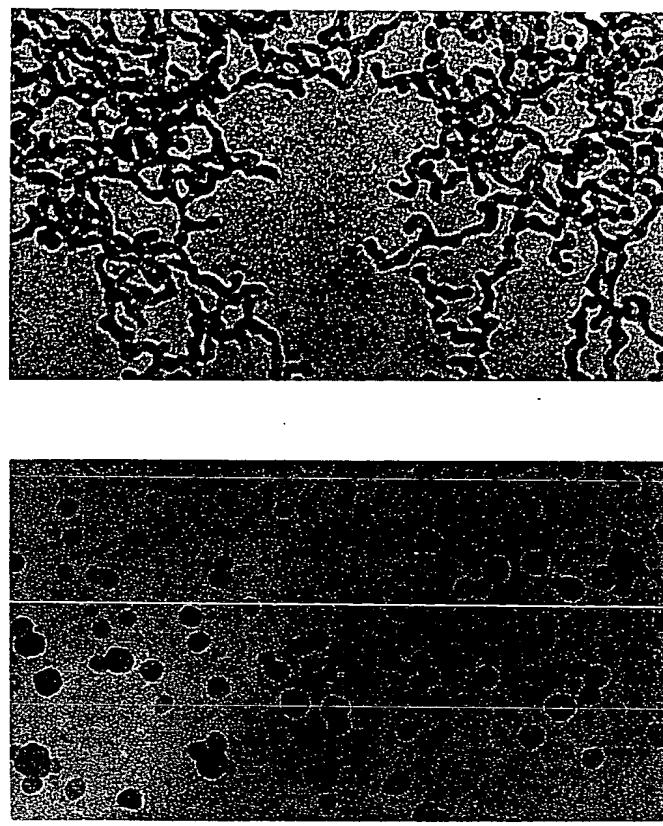


Figure 9. Silica sols with spherical (left) and elongated (right) particles.

Besides varying the shapes of silica sols, the functions of silica sols will be varied in the future. Examples include a sol that gives a film with a high refractive index made up of a composite of silica and titanium oxide; a conductive silica sol whose surface is covered with an electrically conductive oxide or metal; and a porous silica sol that is made from ethyl silicate as the raw material.

On the other hand, in terms of manufacturing processes, the procedures employed will have to be improved continually, to improve the efficiency of the cation-exchange procedure, to manufacture silica sols continuously, and to enhance the efficiency of the concentration processes.

Concluding Remarks

From the 1940s to the 1960s, the fundamental technology for manufacturing silica sols was fully established, and wide variety of silica sol products was developed, mainly owing to the achievements of Iler. From the 1970s to the 1980s, mass production processes were developed to achieve cost reduction to meet large-scale applications. And now, the manufacturing of silica sols is entering a new era. Even in this new era, we will surely continue to formulate our ideas and thoughts on the basis of the valuable research results achieved by Ralph Iler.

3

The Formation and Interfacial Structure of Silica SolS

References

1. Griessbach, R. *Chem. Ztg.* 1933, 57, 253-274.
2. Bird, P. C. U.S. Patent 2,244,325, 1941.
3. Bedtold, M. F.; Snyder, O. E. U.S. Patent 2,574,902, 1951.
4. Alexander, C. B. U.S. Patent 2,750,345, 1956.
5. Iler, R. K. *Colloid Chemistry of Silica and Silicates*; Cornell University Press: Ithaca, NY, 1955.
6. Balhiss, J. H. U.S. Patent 2,614,994-5, 1952.
7. Radczewski, O. E.; Righter, H. *Kolloid-Z.* 1941, 96, 1.
8. Stöber, W.; Fink, A. J. *Colloid Interface Sci.* 1968, 26, 62.
9. Loftman, K. A.; Therepult, J. R. U.S. Patent 2,984,629, 1961.
10. Graham, T. J. *Chem. Soc. London* 1864, 17, 318.
11. Sanchez, M. G. Canadian Patent 586,261, 1959.
12. White, J. F. U.S. Patent 2,375, 1945.
13. Alexander, C. B.; Iler, R. K. U.S. Patent 2,601,235, 1952.
14. Birch, P. G. U.S. Patent 2,244,325, 1941.
15. Alexander, C. B. *J. Am. Chem. Soc.* 1954, 76, 2094.
16. Alexander, C. B.; McWhorter, J. R. U.S. Patent 2,833,724, 1958.
17. Broge, E. C.; Iler, R. K. U.S. Patent 2,680,721, 1954.
18. Chilton, H. T. J. British Patent 1,148,950, 1969.
19. Iler, R. K. U.S. Patent 3,969,266, 1976.
20. Mudrick, M.; Reven, L. E. U.S. Patent 3,342,747, 1967.
21. Akabayashi, H.; Syoji, H. Japanese Patent 288,231, 1961.
22. Iler, R. K. U.S. Patent 2,692,863, 1954.
23. Alexander, C. B. U.S. Patent 2,892,797, 1959.
24. Alexander, C. B.; Bolt, G. H. U.S. Patent 3,007,878, 1961.
25. Akabayashi, H.; Yoshida, A. Japanese Patent 447,161, 1965.
26. Iler, R. K. U.S. Patent 2,668,149, 1952.
27. Yoshida, A. *Chem. Econ. (Jpn.)* 1988, 6, 22.
28. Akabayashi, H.; Yoshida, A. *Kogyo Kagaku Zasshi* 1966, 68, 429.
29. Akabayashi, H.; Yoshida, A. *Kogyo Kagaku Zasshi* 1966, 69, 1832.
30. Broge, E. C. U.S. Patent 2,680,721, 1954.
31. Watanabe, Y.; Ando, M. European Patent Appl. Publication No. A2,0335195, 1989.

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Several techniques, including small-angle neutron scattering (SANS), ultracentrifugation, photon correlation spectroscopy, and ²⁹Si NMR spectroscopy, were used to investigate the nature of the oxide-water interface of silica sols and its significance in the formation and growth of colloidal particles in aqueous solution. These studies were performed with a range of commercial silica sols of different diameters in the range \approx 7-30 nm. When the diameter is small the sols contain a significant proportion of oligomeric silicate species that may be associated at the surface of the particles. For sols of the largest diameter, the relative proportion of oligomers is much smaller. In all the sols the core of the particles has a highly condensed Si-O-Si structure.

THE CLASSIC DESCRIPTION of the structure and mechanisms of formation of silica sols by the hydrolysis and condensation of silicates in aqueous media was given by Iler in 1979 (1). According to Iler, polymerization may occur in essentially three stages: (1) the polymerization of monomers to oligomers and then to primary particles, (2) growth of particles, and (3) particle aggregation to form networks that eventually give rise to a gel

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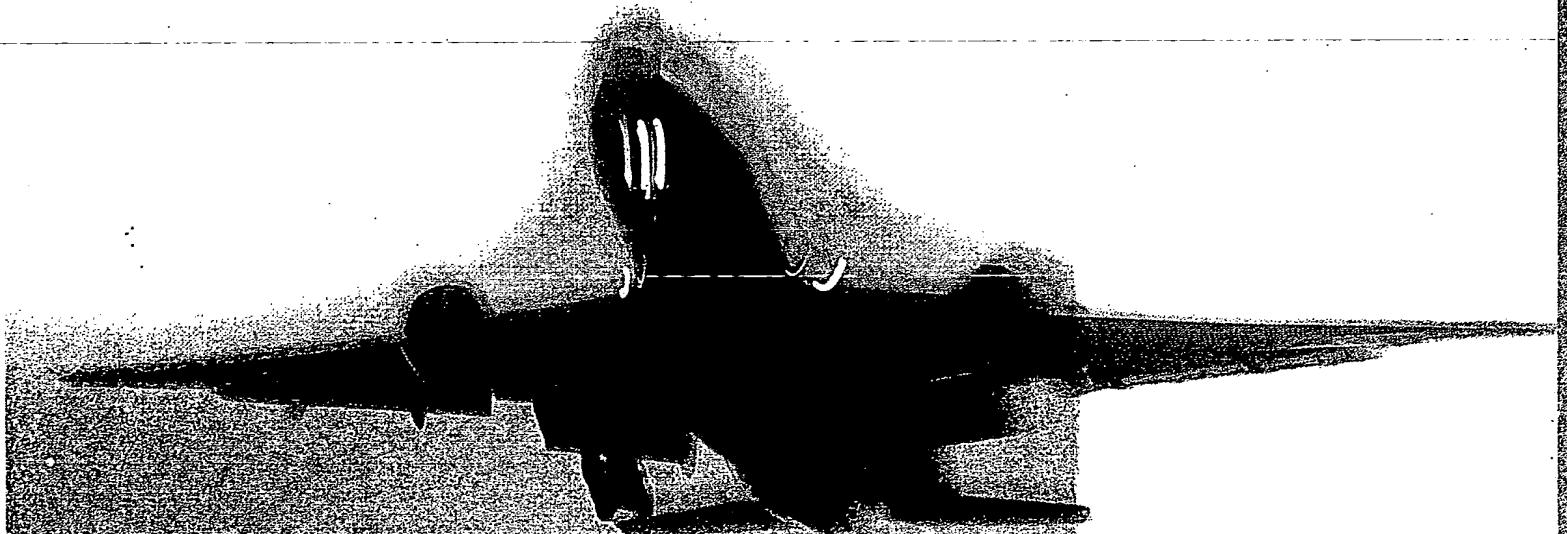
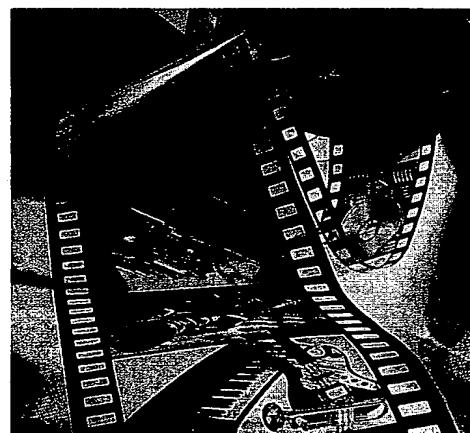
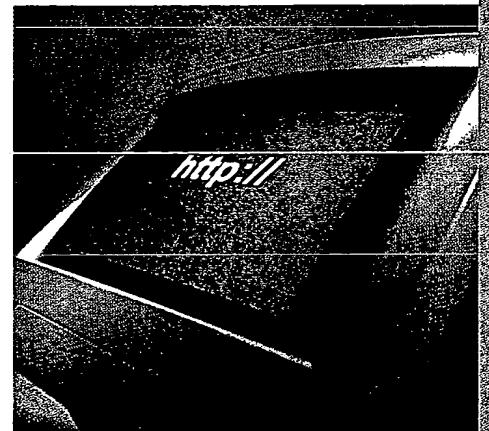
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GRACE Davison

LUDOX®

Colloidal Silica



Properties, Uses, Storages and Handling

Introduction

LUDOX® is aqueous colloidal dispersion of very small silica particles.

They are opalescent to milky white liquids.

Because of their colloidal nature, particles of LUDOX® have large specific surface area which accounts for the novel properties and wide variety of uses.

All grades are produced following proprietary processes and although the chemistry involved is the same, different processes can lead to:

- mono-dispersed, very narrow particle size distribution for LUDOX® (figure A)
- poly-dispersed, broad distribution for LUDOX® P (figure B).

This fundamental difference makes the GRACE range one of the most versatile available worldwide. The end users have shown preference for one or the other depending on the application and their own processes.

Table 1 and 2 show the major characteristics of each individual grade.

Figure A

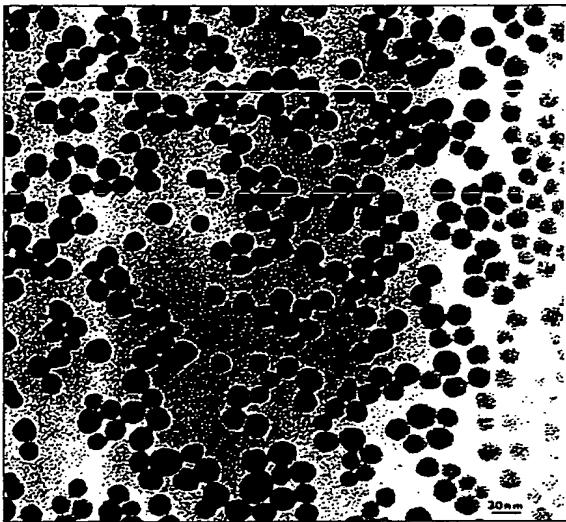
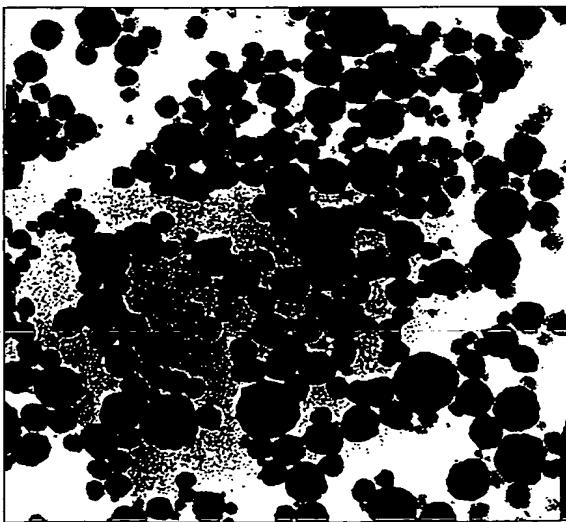


Figure B



LUDOX®

Colloidal Silica

Table 1 – LUDOX® P (Poly-dispersion)

| SSA¹⁾ Particle size | SiO²⁾ content | | Cation | Additive | Grade |
|-------------------------------------------|-------------------------------------|-----|---------------------------------|--------------------------|--------------|
| 230 - 290 / small X | 30% | X30 | Na+ | None EG ²⁾ | X30 X30FS |
| 130- 180 / intermediate T | 40% | T40 | Na+ | None | T40 |
| | | | (NH ₄) ⁺ | None | T40AS |
| 60 - 90 / large W | 30% | W30 | Na+ | None EG ²⁾ | W30 W30FS |
| | 50% | W50 | Na+ | None EG ²⁾ | W50 W50FS |

¹⁾ SSA = Specific surface area (m²/g SiO₂)²⁾ EG = Ethylene glycol (anti-freeze agent)

Table 2 – LUDOX® (Mono-dispersion)

| SSA¹⁾ Particle size | SiO²⁾ content | Conter Ion Surf. coat | Additive | Grade | | |
|-------------------------------------------|-------------------------------------|--------------------------------------|---------------------------------|-----------------------------------------|-----------------|------|
| 320 - 400 / very small SM | 30% | SM30 | Na+ | None | SM30 | |
| | | | (NH ₄) ⁺ | None | SM-AS | |
| | 40% | HS40 | Na+ | None | HS40 | |
| | | | Na+ | EG ²⁾ | HS40FS | |
| | | HS30 | Na+ | None | HS30 | |
| | | | Na+ | EG ²⁾ | HS30F | |
| | | | Na+ | Alkali | HS30HipH | |
| | | | Na+/A1 | None | AM | |
| | | | (NH ₄) ⁺ | None | AS30 | |
| | CL | C1 /A1 | None | CL | | |
| 198 - 258 / small HS | 30% | SK | | Polymer Surfactant | SK | |
| | | | | Polymer | SK-B | |
| | | | None/A1 | High Mw ³ Polymer | SK-R | |
| | | | | High Mw ³ Polymer Surfactant | SK-F | |
| | | | | | | |
| | | | | | | |
| | LS | LS | Na+ | Low Na | LS | |
| | 29 - 155/intermediate AS | 40% | AS40 | (NH ₄) ⁺ | None | AS40 |
| | 110 - 150/intermediate TM | 50% | TM50 | Na+ | None | TM50 |
| | | 45% | | | X ⁴⁾ | CL-X |
| | | 40% | TM40 | Na+ | None | TM40 |
| | | 34% | | N | | TMA |
| | | 30% | | Na+ | X ⁴⁾ | PGE |

¹⁾ SSA = Specific surface area

²⁾ Mw = Molecular weight

³⁾ EG = Ethylene glycol

⁴⁾ X = Proprietary additive (not disclosed)

Table 3 – Typical Properties of LUDOX® Colloidal Silica

| Grades | | | | | | | | |
|------------------------------------------------------|-------------|-------------|-----------|-----------|------------------------|------------------|-----------|-------------|
| | LUDOX® HS40 | LUDOX® HS30 | LUDOX® TM | LUDOX® SM | LUDOX® AM ^a | LUDOX® AS | LUDOX® LS | LUDOX® CL-X |
| Stabilizing counter ion | Sodium | Sodium | Sodium | Sodium | Sodium | Ammonium | Sodium | Sodium |
| Particle charge | Negative | Negative | Negative | Negative | Negative | Negative | Negative | Negative |
| Specific surface area, m ² /g | 220 | 220 | 140 | 345 | 220 | 135 | 215 | 130 |
| Silica (as SiO ₂), wt % | 40 | 30 | 50 | 30 | 30 ^b | 40 | 30 | 46 |
| pH (25 °C) | 9.7 | 9.8 | 9.0 | 10.0 | 8.9 | 9.1 | 8.2 | 9.1 |
| Titratable alkali (as Na ₂ O), wt % | 0.41 | 0.32 | 0.21 | 0.56 | 0.24 | c | 0.10 | 0.19 |
| SiO ₂ /Na ₂ O (by wt) | 95 | 95 | 225 | 50 | 125 | 220 ^d | 270 | 230 |
| Chlorides (as NaCl), wt % | 0.01 | 0.01 | 0.03 | 0.01 | 0.007 | 0.005 | 0.003 | 0.03 |
| Sulfates (as Na ₂ SO ₄), wt % | 0.03 | 0.03 | 0.08 | 0.04 | 0.006 | 0.007 | 0.003 | 0.07 |
| Viscosity (25 °C), cP, (mPa•s) | 16 | 4 | 40 | 5.5 | 7 | 11 | 8 | 17 |
| Wt per gallon (25 °C), lb | 10.8 | 10.1 | 11.6 | 10.1 | 10.0 | 10.7 | 10.0 | 11.4 |
| Specific gravity (25 °C) | 1.31 | 1.21 | 1.40 | 1.22 | 1.21 | 1.30 | 1.21 | 1.37 |

^a Surface modified with aluminate ions

^b Concentration includes SiO₂ + Al₂O₃

^c Sol contains 0.16 % NH₃ and 0.08 % Na₂O (occluded)

^d SiO₂/NH₃

The above table gives typical properties based on historical production performance. GRACE does not make any express or implied warranty that these products will continue to have these properties.